Aluminum Dichloride and Dibromide. Preparation, Spectroscopic (Including Matrix Isolation) Study, Reactions, and Role (Together with Alkyl(aryl)aluminum Monohalides) in the Preparation of Organoaluminum Compounds

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Abstract: Anhydrous aluminum trichloride or bromide when heated in a 2:1 molar ratio with aluminum powder as a suspension in dry *n*-heptane or methylcyclohexane was found to be partially reduced to aluminum dichloride or dibromide. Ultrasound treatment (sonication) significantly promotes the reaction. Aluminum dichloride in higher purity was obtained by the reaction of gaseous aluminum trichloride with aluminum metal in a high-vacuum reactor, allowing subsequent investigation by IR spectroscopy. An aluminum sub-halide of the form $Al_2(i\text{-}Bu)_{4-x}Cl_x$ was also prepared through the reaction of tetraisobutyldialane and HCl at low temperature. Both materials were investigated by IR spectroscopy and compared to $AlCl_2$ prepared and isolated through the codeposition of aluminum atoms and molecular chlorine in a solid argon matrix. The matrix study characterized $AlCl_2$ together with AlCl and $AlCl_3$, which were also formed in the system. The paramagnetic aluminum dihalides, i.e. $AlCl_2$ and $AlBr_2$, are associated in the condensed state (except under matrix isolation conditions where they are monomeric). An ESR study of the pyridinium complex of $AlCl_2$ was carried out and showed its paramagnetic nature. In the present study, for simplicity, the reactions of aluminum dihalides are considered as those of the dimers but could involve higher associated oligomers. MNDO calculations on the heats of formation of several possible isomeric structures of Al_2Cl_4 indicate the preference for both halogen bridging and significant Al–Al bonding in the dimer. Reaction of $AlCl_3$ + Al with ethylene, the Hall and Nash reaction, was reinvestigated by ^{13}C and ^{27}Al NMR spectroscopy. The reaction was found to give, besides ethylaluminum sesquichloride, 1,2- and 1,1-bis(dichloroaluminio)ethanes. Cyclohexene in a similar reaction gives, although less readily, 1,2-bis(dichloroaluminio)cyclohexane. The reactions are indicative of addition of $(AlCl_2)_2$ to the olefins. Alkyl- and arylaluminum monohalides are intermediately formed in the reaction of alkyl halides or halobenzenes with active aluminum powder. These divalent aluminum halides are also considered to be dimeric in nature and immediately react with excess of the alkyl (aryl) halides to form the corresponding sesquihalides. In contrast, aluminum dihalides formed in the aluminum trihalide–aluminum metal systems react with alkyl or aryl halides to give alkyl(aryl)aluminum dihalides. Sonication was found to significantly promote these reactions.

In 1877 Friedel and Crafts first reported[1] the use of anhydrous aluminum trichloride as a catalyst in organic synthesis. The aluminum trichloride was a sample of the material used in preparing, via reduction, the first ingot of aluminum metal. Today, there is renewed interest in obtaining aluminum by the reduction of aluminum trichloride. The reductive dechlorination of aluminum trichloride to metallic aluminum must proceed through lower valency forms such as Al(I) and Al(II). Until now, however, only some studies of gaseous aluminum sub-chlorides were reported. Aluminum sub-chlorides, so far, have not been reported in the condensed state, nor has their possible role been recognized in the formation of organoalanes.

Aluminum monochloride is formed in the reaction of aluminum with aluminum trichloride at 1100 K.[2] Subsequent theoretical calculations have shown that AlCl may further react with $AlCl_3$ to give $AlCl_2$,[3] a reaction comparable to the insertion of BF into BF_3 giving B_2F_4.[4]

$$AlCl_3 + 2Al \rightarrow 3AlCl$$

$$AlCl + AlCl_3 \rightarrow 2AlCl_2$$
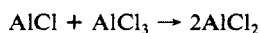
Combining our long-standing interest on one hand in the chemistry of aluminum trichloride and related Friedel–Crafts systems and matrix isolation studies of molecules produced by hot-atom chemistry on the other, we now report the preparation and study of aluminum dihalides, including some of their characteristic reactions and their role (together with that of alkyl-

(aryl)aluminum monohalides) in the formation of organoaluminum compounds.

Results and Discussion

Preparation of Aluminum Dichloride and Dibromide. When doubly sublimed anhydrous aluminum trichloride and aluminum powder of high purity in a molar ratio of 2:1 are heated in a pressure autoclave under nitrogen or argon atmosphere in dry heptane or methylcyclohexane at 120 °C for 5–10 h, after cooling to room temperature, depressurizing, and removing the supernatant solvent, the remaining grayish residue is highly reactive to air and moisture. It still contains some Al metal and $AlCl_3$, and no ready isolation of product AlX_2 is possible. Aluminum dichloride ($AlCl_2$) of higher purity was subsequently obtained by reacting gaseous $AlCl_3$ with aluminum metal under high vacuum at 580 °C. A low-temperature route to aluminum sub-chloride (mixed with other materials) was realized through the reaction of tetraisobutyldialane and HCl at –78 °C.

$$2AlCl_3 + Al \rightleftharpoons 3AlCl_2$$

Aluminum dihalides are relatively unstable and even at room temperature tend to disproportionate to some degree to aluminum trihalides and metallic aluminum. Aluminum dihalides are highly electron-deficient paramagnetic molecules and therefore inevitably

(1) (a) Friedel, C.; Crafts, J. M. *C. R. Hebd. Seances Acad. Sci.* **1877,** *84,* 1392. (b) For a historical background, see: Olah, G. A. *Friedel–Crafts Chemistry;* Wiley-Interscience: New York, 1973; pp 1–24.
(2) Rao, D. B.; Dadape, V. V. *J. Phys. Chem.* **1966,** *70,* 1349.
(3) Chai, B. J.; Ko, H. C.; Greenbaum, M. A.; Farber, M. *J. Phys. Chem.* **1967,** *71,* 3331.
(4) Timms, P. L. *Acc. Chem. Res.* **1973,** *6,* 118.

[†] University of Southern California.
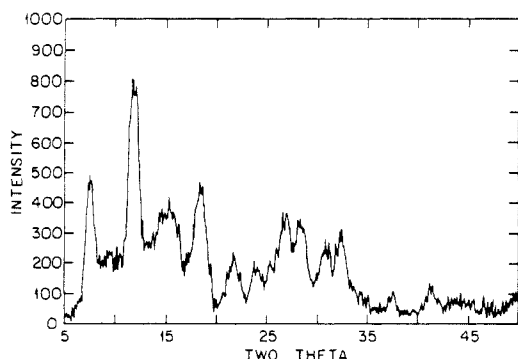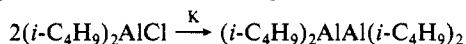[‡] University of Alabama.
[§] University of Virginia.

Figure 1. X-ray powder diffraction pattern of $AlCl_2$ (from Al_2Cl_6 + Al).

Figure 2. Matrix IR spectra of Al atoms with Cl_2 at (a) 120:1 Cl_2:Al and (b) 60:1. Inset shows the 575–555-cm^{-1} region of 120:1 sample in more detail to enhance the ^{35}Cl, ^{35}Cl isotopic splitting. Bands labeled M, D, T, and H refer to aluminum mono-, di-, tri-, and hexachloride, and DC and TC refer to complexes of di- and trichloride with either Cl_2 and/or N_2 impurity.

associate in the condensed state. Association can be through halogen bridging, Al–Al bonding (similar to the B–B bonding in tetrahalodiboranes[5]), or both. Aluminum dihalides are relatively insoluble in noncoordinating saturated hydrocarbon solvents, and hence in these media no exact degree of association could be ascertained. For simplicity in the context of chemistry discussed in this paper, aluminum dihalides are depicted as dimers, although in fact they may be in cases higher associated oligomers.

Aluminum dichloride was also prepared and isolated by low-temperature argon matrix codeposition of aluminum atoms and molecular chlorine and studied by infrared spectroscopy (vide infra). Under these conditions we are dealing with a monomeric species. $AlCl_3$ and $AlCl$ are also present in the matrix studies, which allow a suggestion for the mechanism of the formation of $AlCl_2$ from Al atoms and Cl_2 molecules. It should be noted that tetraisobutyldialane[6] is so far the only well-defined compound containing an Al–Al bond. It was prepared by the reduction of diisobutylaluminum chloride with potassium metal.

$$2(i\text{-}C_4H_9)_2AlCl \xrightarrow{K} (i\text{-}C_4H_9)_2AlAl(i\text{-}C_4H_9)_2$$

It is also of interest that tetracarbonyldialane was also recently indicated in a spectroscopic study.[7] When tetraisobutyldialane was reacted with HCl gas in a hexane solution at -78 °C, both Al–C and Al–Al bond protolysis occurs contrary to an earlier report.[8a] However, no pure Al_2Cl_4 species was obtained in the reaction.

IR Spectroscopic Studies. The product mixture from the re-action of gaseous $AlCl_3$ and Al metal was handled with extreme care in an efficient drybox under dry argon atmosphere. IR spectroscopy of the product mixture (as KBr pellet) showed two distinct absorption bands at 619 and 561 cm^{-1}. The higher energy band at 619 cm^{-1} is that of $AlCl_3$ as confirmed by comparison with the spectrum of authentic $AlCl_3$ under identical conditions. The lower energy band at 561 cm^{-1}, which is absent in the $AlCl_3$ spectrum, is attributed to $AlCl_2$ (in its associated form). The material from the tetraisobutyldialane and HCl reaction has an IR spectrum that is more complicated than that for the Al + $AlCl_3$ high-temperature material. There were peaks near 2700, 1450, 801, 692, and 485 cm^{-1} as well as a shoulder near the expected energy of 560 cm^{-1}.

The composition of this material must be due, in part, to $Al_2(i\text{-}Bu)_{4-x}Cl_x$ ($x \leq 4$) as it readily adds to cyclohexene (vide infra). The retention of the Al–Al bond in the product is a new discovery for this reaction.[6a,8] At higher temperature, the Al–Al bond is cleaved preferentially. At lower temperature, the reaction is similar to the reaction of 1,1-bis(dichloroaluminio)ethane with HCl where C–Al bonds react with Cl eventually liberating ethane (vide infra). To support the structure of aluminum sub-chloride from Al + $AlCl_3$, X-ray powder diffraction was also carried out. The pattern was distinctly different from those of $AlCl_3$ and also
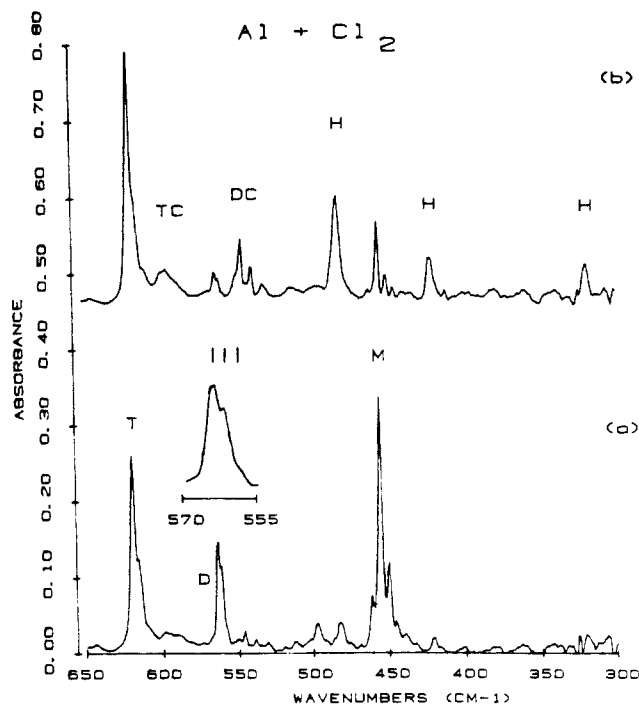
Al metal (see Figure 1). Structural studies using the X-ray powder diffraction are continuing.

For a more in-depth study of the IR spectrum of aluminum dichloride, we also undertook a low-temperature argon matrix isolation infrared study of the reaction of hot Al atoms with molecular chlorine (Figure 2). Mixtures of Cl_2 and argon gas in mole ratios between 1:60 and 1:240 were codeposited with aluminum atoms evaporated from solid aluminum metal sample, with techniques previously used by one of us.

Deposition of aluminum atoms with Cl_2 gave rise to several product absorptions in the 650–300-cm^{-1} region. Relative intensities of these new bands varied both with Al and Cl_2 concentrations and also on annealing the matrix.

Basically, at low Al and Cl_2 concentrations, three product bands were observed, each exhibiting chlorine isotopic splittings. The absorption at 620 cm^{-1} showing splittings consistent with three equivalent Cl atoms is identical with that already assigned to $AlCl_3$ (T) in solid argon produced by superheating Al_2Cl_6 vapor.[8b,9] This band is near the 610-cm^{-1} value assigned to $AlCl_3$ in the gas phase.[10] The band at 455 cm^{-1} shows a 3:1 isotopic ratio and is very close to the gas-phase fundamental for aluminum mono-chloride $AlCl$ (477 cm^{-1});[11] matrix shifts for metal chlorides are typically to the red, owing to dipole-induced dipole interaction with the matrix.[10] The 455.2–449.6-cm^{-1} splitting is in agreement (± 0.1 cm^{-1}) with the calculated harmonic oscillator isotopic shift for $AlCl$ diatomic, and accordingly, the 455-cm^{-1} band can be assigned to $AlCl$ (M). The bands around 560 cm^{-1} are weaker, show approximately 9:6:1 isotopic splitting relative intensities (as exhibited in Figure 2), and raise the possibility of assignment to the dichloride $AlCl_2$ (D). Other bands were also observed, but they become more pronounced at higher concentrations and also after annealing the matrix and can be assigned to higher complexes or clusters like Al_2Cl_6 (H).[3–5] Figure 2 shows the Al and Cl_2 spectrum (a) at 120:1 and (b) at 60:1. At higher Cl_2 concentration,

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Table I. Infrared Absorptions (cm^{-1}) Observed in an Argon Matrix with Cl_2 (120:1) and Al Atoms at 12 K

posn, cm^{-1}	absorbance[a]	assignment[b]
619.2	0.26 (−)	$AlCl_3$ various isotopes[c] (T)
615.2	0.13 (−)	
612.5	0.06 (−)	
599.0	0.02 (+)	complexes of $AlCl_3$[c] with Cl_2 and/or N_2 (TC)
594.0	0.01 (+)	
587.0	0.01 (+)	
563.6	0.16 (−)	$AlCl_2$ ($^{35}Cl^{35}Cl$)
561.3	0.12 (−)	(D) ($^{35}Cl^{37}Cl$)
558.3	0.02 (−)	($^{37}Cl^{37}Cl$)
546.0	0.01 (+)	complexes of $AlCl_2$ with Cl_2 and/or N_2 (DC)
538.5	0.01 (+)	
530.0	0.01 (+)	
496	0.04 (+) (br)	Al_2Cl_6 (H)[c]
482	0.04 (+) (br)	U (unidentified)
461.0	0.08 (no)	U
455.2	0.34 (−)	$Al^{35}Cl$ (M)[d]
449.6	0.12 (−)	$Al^{37}Cl$ (M)
421	0.02 (+) (br)	Al_2Cl_6 (H)[c]
320	0.02 (+) (br)	Al_2Cl_6 (H)

[a] + and − refer to the band-growth behavior on annealing. [b] M, D, T, and H refer to aluminum mono-, di-, tri-, and hexachloride, respectively; DC and TC refer to dichloride and trichloride complexes. [c] From ref 6 and 7. [d] Gas-phase value from ref 9 is 477 cm^{-1}.

cluster bands Al_2Cl_6 (H), TC (trichloride complex), and DC (dichloride complex) increase in intensity, and both the monochloride (M) and dichloride (D) bands decrease relatively. In actuality, increasing Cl_2 concentration increased the yield of both monochloride and dichloride up to 120:1 ($Al:Cl_2$) ratio after which the yield decreased, all relative to trichloride. The same trend was observed for Al concentration. Increases of Al concentration (vapor pressure) increased the yield of monochloride and dichloride relative to trichloride. Bands designated by TC and DC are believed to be due to complexes of trichloride and dichloride with either Cl_2 or N_2 impurities as already discussed by other workers.[6,7] Table I gives the band positions and their assignments.

The definitive identification of the known aluminum–chlorine species $AlCl_3$ and $AlCl$ and the new $AlCl_2$ molecule provides basis for a mechanism of the reaction of Al atoms and Cl_2 molecules on the surface of the matrix during codeposition of these elements. The observation of $AlCl$ as the strongest absorption under dilute conditions shows that $AlCl$ is the primary reaction product (eq 1), particularly in view of the fact that force constants of the

$$Al + Cl_2 \rightarrow AlCl + Cl \tag{1}$$
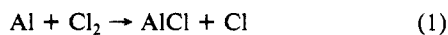
antisymmetric Al–Cl stretching modes for $AlCl_2$ and $AlCl_3$ are expected to be higher. The dichloride is probably formed by secondary reaction 2, and the trichloride can be formed by secondary reactions 3 and 4. Al_2Cl_6 is formed by direct dimerization of $AlCl_3$.

$$Cl + AlCl \rightarrow ClAlCl \tag{2}$$

$$Cl + AlCl_2 \rightarrow AlCl_3 \tag{3}$$

$$Cl_2 + AlCl \rightarrow AlCl_3 \tag{4}$$
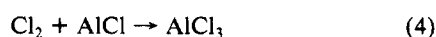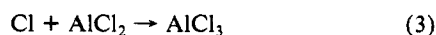
$AlCl_2$ is of particular interest here since no divalent aluminum compound has previously been examined spectroscopically. From reaction 2, it is expected that $AlCl_2$ is an obtusely bent molecule. Indeed, the $Al^{35}Cl_2-Al^{37}Cl_2$ shift of 563.6 to 558.3 cm^{-1} fits accurately by the antisymmetric stretching mode, ν_3, of $AlCl_2$ with a 120° valence angle, using the antisymmetric mode G matrix element ($\mu_{Al} + \mu_{Cl} - \mu_{Al} \cos \alpha$). However, an approximately equilateral triangular structure is theoretically possible, as the Cl_2 and $AlCl$ internuclear distances[11] in the diatomics are 1.99 and 2.13 Å, respectively. Furthermore, $Al^+Cl_2^-$, if formed, would be such a species with a side dimension near 2.2 Å, and its ν_2 G matrix element is identical with the ν_3 element above. The alkali-metal dichloride species have been studied extensively.[12] The Cl_2

Table II. Calculated Heats of Formation for Possible Al_2Cl_4 and Al_2H_4 Isomers

| geometry			hydrides		chlorides	
			H_f	rel	*H_f*	rel
X_2Al-X_2Al	C_{2v}	1	47.3	0	−185.0	−8.3
$XAl-X_3-Al$	C_{3v}	2	54.6	7.3	−176.7	0
$X_2Al-AlX_2$	D_{2d}	3	60.9	13.6	−165.2	11.5
$X_2Al-AlX_2$	D_{2h}	4	63.8	16.5	−163.4	13.3
$X_2Al-X-AlX$	C_s	5	65.3	18.0	−165.9	10.8
$X_3Al-Al-X$	C_s	6	65.6	18.3	−166.5	10.2
$XAl-X_2-AlX$	C_{2v}	7	92.9	45.6	−149.3	26.7

concentration dependence for the $AlCl_2$ product argues, however, for a two-step mechanism (eq 1 and 2) rather than the single-step $Al^+Cl_2^-$ species. Although the ν_2 mode of $Al^+Cl_2^-$ has the same isotopic dependence, this fundamental would be much lower in frequency. This ν_2 mode for $Na^+Cl_2^-$ has been predicted at 270 cm^{-1}.[12]

Finally, comparison of the ν_3 fundamentals for $MgCl_2$, $AlCl_2$, and $SiCl_2$ shows that the observed 564-cm^{-1} band is due to obtuse bent ClAlCl. These metal chlorides show a trend: $MgCl_2$ (linear, ν_3 597 cm^{-1}, gas, ν_3 580 cm^{-1}, solid argon)[13,14] $AlCl_2$ (bent, 120–140°, ν_3 564 cm^{-1}, solid argon), and $SiCl_2$ (bent, 110 ± 10°, ν_3 513 cm^{-1}, solid argon).[15] It is expected that this series of molecules, $MgCl_2$, $AlCl_2$, and $SiCl_2$, will exhibit similar bond strengths and decreasing valence angles, and these ν_3 modes support this postulate. The close agreement of ν_3 fundamentals for $MgCl_2$, $AlCl_2$, and $SiCl_2$ substantiates this first identification of the divalent aluminum species.

It is important to note that, in the matrix, $AlCl_2$ is assigned as a monomer, while, in the Al + $AlCl_3$ reaction, the product is not ESR active and thus cannot be monomeric. Therefore, the proximity of the IR band in a sample of the Al + $AlCl_3$ reaction (561 cm^{-1}) to that of the matrix (564 cm^{-1}) when the two species are clearly in different forms must be explained.

To address this problem, we have compared the IR spectra of $AlCl_3$ monomer and dimer.[16] The higher energy region of the spectra (600–700 cm^{-1}) is essentially identical. This band is assigned to the Al–Cl stretch and is apparently not sensitive to the coordination number of the metal. Similarly, we have assigned the bands at 561 and 564 cm^{-1} to the antisymmetric Al–Cl stretch of $AlCl_2$. Thus, through the precedent with $AlCl_3$, one should expect a similarity in the spectra of monomeric and condensed $AlCl_2$.

Theoretical Study of the Structure of the Aluminum Dichloride Dimer. In the absence of detailed structural data, calculation of the heats of formation of possible structures **1–7** of the aluminum dichloride dimers ($(AlCl_2)_2$) by Dewar's MNDO method[17] gives some indication of the preferred geometries.
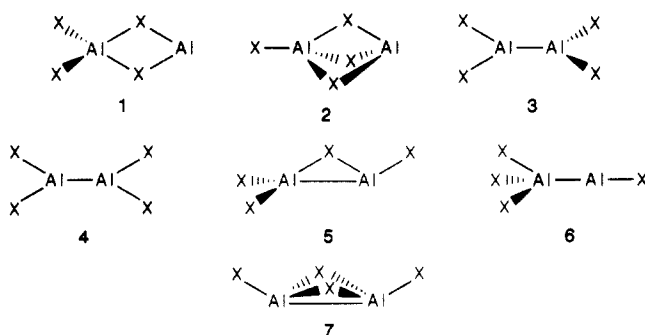
For comparison (in Table II), the related heats of formation of the corresponding hydrides (Al_2H_4)[18] are also shown.

(12) Howard, W. F., Jr.; Andrews, L. *Inorg. Chem.* **1975**, *14*, 767.
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(17) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899, 4907. GCBE Publication 455, Department of Chemistry, Indiana University, Bloomington, IN 47405.

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Al_2Cl_4 could also have ionic nature, $Al^+[AlCl_4]^-$, similar to the known ionic structures of Ga_2X_4 and In_2X_4 (i.e. $M^+[MX_4]^-$). This contrasts with the boron–boron bonded structure of B_2Cl_4, which is covalent.[19] The MNDO calculations on Al_2Cl_4 indicate a rather flat potential energy surface, with structures **1** and **2** being energetically favored. This represents either an edge-on or face-on complexation of Al^+ with $AlCl_4^-$. Consequently, the initial interaction of Al_2Cl_4 with π-systems such as ethylene (vide infra) could be a donor–acceptor interaction of Al^+ in **1** with the π-bond of ethylene. On the other hand, the preferred Al–Al-bonded structure **7** could also interact with ethylene in a side-on fashion. As it was observed that Ga_2X_4 and In_2X_4 do not react with ethylene to provide bis(dihalogallio)- or bis(dihaloindio)ethane, the ionic nature of Al_2X_4 must be limited. Thus, Al_2X_4 structures must be viewed different from the ionic structure (i.e. $Al^+AlX_4^-$). The AlX_3–AlX complexes **5** and **6**, as well as AlX_2 dimers **3** and **7** in their interaction with ethylene, would involve initial complexation of one Al atom with the π-bond followed by structural rearrangement to the bis(dihaloaluminio)ethane products (vide infra). The tetrahalodialane form **4** could also react with ethylene in a 2 + 2 concerted fashion (similar to the reaction of its boron analogue[19]).

Even with the limitations of the MNDO method, data clearly show the tendency for both halogen-bridging as well as significant Al–Al-bonding character in the Al_2X_4 dimer.

Chemical Reactivity. Addition to Olefins. Hall and Nash in 1936 reported that $AlCl_3$ and Al metal, when heated with ethylene without any solvent, give ethylaluminum sesquichloride.[20a,b]

$$3CH_2\!\!=\!\!CH_2 + AlCl_3 + Al + 1.5H_2 \xrightarrow[\substack{60\ \text{atm}}]{155\ °C}$$
$$(C_2H_5)_2AlCl\cdot C_2H_5AlCl_2$$
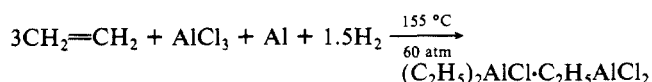
This remarkable reaction is a complex process where Friedel–Crafts oligomerization and cyclization liberate sufficient hydrogen needed for the formation of ethylaluminum halides. Subsequently, Ruthruff[21b] was able to improve the Hall and Nash reaction by performing it under hydrogen pressure.

We have reinvestigated the Hall and Nash reaction with various $AlCl_3$ to Al ratios and studied the reaction mixture before workup by ^{13}C and ^{27}Al NMR spectroscopy.[20c] It was observed that, besides ethylaluminum chlorides, 1,2- and 1,1-bis(dichloroaluminio)ethane are also formed (the latter present probably as oligomers). This observation led us to a more detailed investigation of the reaction of AlX_3 + Al with ethylene.

Heating a mixture of $AlCl_3$ or $AlBr_3$ and Al metal in either heptane or methylcyclohexane solvent under ethylene pressure in an autoclave results in the formation of ethylaluminum halides, with ethylaluminum dihalides predominating. Besides ethylaluminum dihalides, *gem*-1,1-bis(dihaloaluminio)ethane **9** as well as small amount of 1,2-bis(dihaloaluminio)ethane **8** were obtained. After prolonged reaction time, **8** appears to quantitatively isomerize to the more stable isomer **9**. The compound **9** was isolated as an off-color solid (see the Experimental Section).
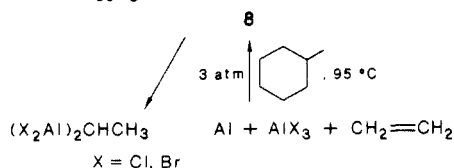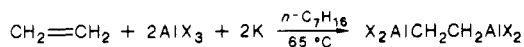
$$CH_2\!\!=\!\!CH_2 + 2AlX_3 + 2K \xrightarrow[65\ °C]{n\text{-}C_7H_{16}} X_2AlCH_2CH_2AlX_2$$
8

$(X_2Al)_2CHCH_3 \qquad Al + AlX_3 + CH_2\!\!=\!\!CH_2$

X = Cl, Br

(18) Ab initio calculations of the Al_2H_4 isomers are data by: Lammertsma, K.; Schleyer, P. v. R., private communication.

(19) Schmidbaur, H.; Zafiropoulos, T.; Bublak, W.; Burkert, P.; Köhler, F. H. *Z. Naturforsch., A: Phys., Phys. Chem., Kosmophys.* **1986**, *41A*, 315.

(20) (a) Hall, F. C.; Nash, A. W. *J. Inst. Pt. Technol.* **1937**, *23*, 679. (b) Hall, F. C.; Nash, A. W. *J. Inst. Pet. Technol.* **1938**, *24*, 471. (c) We were able to reproduce the Hall and Nash reaction under Fischer's condition (using heptane solvent) in the absence of $TiCl_4$ catalyst.
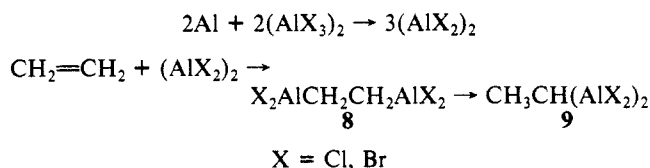
(21) (a) Martin, H.; Bretinger, H.; Furbach, F. *Angew. Chem.* **1985**, *97*, 323. Martin, H.; Bretinger, H. *Z. Naturforsch.* **1985**, *40*, 182. (b) Ruthruff, R. F. U.S. Patent 2 271 956, 1942; *Chem. Abstr.* **1942**, *36*, 3513.

Table III. NMR Spectroscopic Data of Bis(dichloroaluminio)ethanes

compd	^{1}H NMR,[a] δ	^{13}C NMR,[b] δ	^{27}Al NMR,[c] δ
8		5.2 (t)	35 (br)
9 (Cl)	-0.6 (q, J_{H-H} = 7 Hz)	-1.9 (d)	-23 (br)
9 (Br)	1.52 (d, J_{H-H} = 7 Hz)	10.0 (q)	
	-0.4 (q)	~-1 (br)	~-20 (vbr)
	1.6 (d)	9.13 (q)	

[a,b] In ppm from tetramethylsilane signal. [c] In ppm from $AlCl_3(CH_3CN)_6$ complex.

It was Kooyman et al.[22] and Eidt,[23] respectively, who first reported that when ethylene was treated with aluminum trichloride in the presence of a reducing metal such as potassium or aluminum under relatively mild conditions [95 °C (3 atm)], 1,2-bis(dichloroaluminio)ethane **(8)** was obtained, in the former case as the monomeric ether complex and in the latter case in its oligomeric form. No structural or spectroscopic proof for **3** was, however, offered by these earlier studies. Martin et al.[21a,b] have recently reported similar studies with the $AlCl_3$ + Al system and obtained 1,2-bis(dichloroaluminio)ethane. In our studies (under all reaction conditions), the major product obtained was always **9** and not **8**.

The structure of bis(dichloroaluminio)ethanes **8** and **9** was confirmed by ^{1}H, ^{13}C, and [27]Al spectroscopy in THF-d_8 or heptane solution, respectively, at -60 °C (see Table III), as well as by quenching experiments.

Deuteriolysis of **9** gives 1,1-dideuterioethane, carboxylation methylmalonic acid, and mercuration with mercuric chloride 1,1-bis(chloromercurio)ethane, respectively.
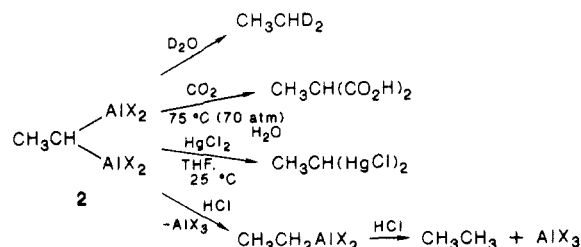
The compound **9** also reacts with dry hydrogen chloride to give ethylaluminum dichloride and aluminum trichloride. With excess HCl, however, ethane and aluminum trichloride are formed. A heptane solution of **9** with added $TiCl_4$ was found to polymerize ethylene to high-density linear polyethylene.[24] The Hall and Nash reaction mixture upon addition of $TiCl_4$ gave similar results. It should be mentioned that M. Fischer in 1943 reported[25] the polymerization of ethylene with Al + $AlCl_3$ and $TiCl_4$ to give solid polyethylene. The nature of the polymer was, however, not characterized, nor was a mechanism suggested for the reaction. A reinvestigation of the reaction with careful temperature control showed that the product obtained, besides Friedel–Crafts oil resulting from $AlCl_3$-catalyzed oligomerization, is linear high-density polyethylene.[24] Consequently, Fischer's reaction can be considered as a direct forerunner to Ziegler–Natta coordination polymerization since the in situ formed ethylaluminum chlorides lead to the active Ziegler catalyst with $TiCl_4$. Besides Al, other reducing metals such as K, Na, Mg, and Zn act in a similar fashion under Fischer's conditions.[24]

The formation of **8** from ethylene and AlX_3 + Al is indicative of the intermediate formation of aluminum dihalides, which in their dimeric form add to ethylene to give **8**, which subsequently isomerizes to the more stable isomer **9**. This was further substantiated when ethylene was reacted with prepared $(AlCl_2)_2$ from the reaction of $AlCl_3$ + Al.

(22) Helden, v. R.; Braendlin, H. P.; Bickel, A. F.; Kooyman, E. C. *Tetrahedron Lett.* **1959**, *12*, 24.
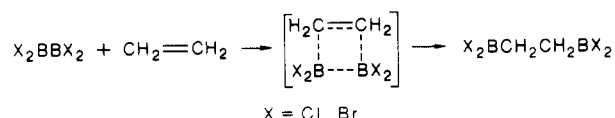
(23) Eidt, S. H. Ger. Offen. 2 535 591; *Chem. Abstr.* **1975**, *85*, 21601s; Br. Patent 1 455 406, 1976.

(24) Olah, G. A.; Bruce, M.; Louet, F.; Farnia, M.; Farooq, O.; Prakash, G. K. S.; Welch, J.; Koenig, J. L. *Macromolecules* **1987**, *20*, 2972.

(25) Fischer, M. Ger. Offen. 874 215 (applied for Dec 18, 1943; granted March 12, 1953).

$$2Al + 2(AlX_3)_2 \rightarrow 3(AlX_2)_2$$

$$CH_2=CH_2 + (AlX_2)_2 \rightarrow$$
$$\underset{\textbf{8}}{X_2AlCH_2CH_2AlX_2} \rightarrow \underset{\textbf{9}}{CH_3CH(AlX_2)_2}$$

$$X = Cl, Br$$

Dimeric dihaloalanes in their tetrahalodialane form are analogous to the well-known tetrahalodiboranes, which react with olefins[5] in a stereospecific cis fashion, clearly indicative of a concerted (2 + 2)-type process.

$$X_2BBX_2 + CH_2=CH_2 \longrightarrow \begin{bmatrix} H_2C---CH_2 \\ | \quad\quad | \\ X_2B---BX_2 \end{bmatrix} \longrightarrow X_2BCH_2CH_2BX_2$$

$$X = Cl, Br$$

Similarly, we have also attempted to obtain bis(dihalogallio)-ethanes from ethylene with Ga + GaX₃ and Ga₂X₄ under related conditions. However, all our attempts were unsuccessful, indicating the previously discussed ionic nature of $Ga^+GaX_4^-$.

Reaction of cyclohexene with AlBr₃ and K at room temperature for 12–18 h gave an oily liquid as well as a dark solid. Hydrolysis of the oil gave cyclohexene and lower oligomers (in 1:2 ratio) along with 4.5% cyclohexane. Control experiments with AlBr₃ alone (in the absence of a reducing metal) also gave some cyclohexane ($\approx$2%) from acid-catalyzed processes. However, preheating of a mixture AlBr₃ and K and subsequently introducing cyclohexene gave a product that upon D₂O quench yielded an 11% yield of cyclohexane-*1,2-d₂* (based on GC-MS analysis). This result clearly indicates the formation of bis(dibromoaluminio)cyclohexane in competition with oligomerization/cracking of cyclohexene by excess AlBr₃.
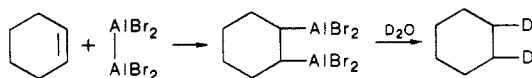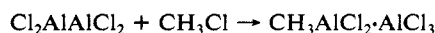

The Al–AlCl₃ system was also found to react with cyclohexene similarly. Initial treatment of the Al and AlCl₃ mixture under sonication followed by heating for several hours and then reacting with cyclohexene gave a reaction product that upon quenching with D₂O gives cyclohexane-*1,2-d₂* in 14% yield (GC-MS). ²H NMR studies of the product also show the formation of 1,2-di-deuteriocyclohexane. Similar results were also obtained with the reaction product of tetraisobutyldialane with HCl gas at low temperature. The product also readily reacts with cyclohexene to form the 1,2-adduct.

Reactions with Alkyl or Aryl Halides. Methyl and ethyl halides are well-known to react with aluminum metal to give alkyl-aluminum sesquihalides.[26]

$$3RX + 2Al \rightarrow R_2AlX_2RAlX_2$$
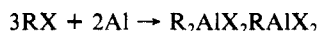
The mechanism of the reaction so far has not been established. Consequently, we undertook a study to establish the mechanism and also to study the reactions of alkyl chlorides with the AlCl₃ + Al system.

AlCl₃ and Al prereacted as discussed previously giving $(AlCl_2)_2$ when allowed to react with methyl chloride give methylaluminum dichloride exclusively. Methyl chloride is assisted in the reaction by complexation with AlCl₃, which increases its polarity and electrophilic nature.

$$Cl_2AlAlCl_2 + CH_3Cl \rightarrow CH_3AlCl_2 \cdot AlCl_3$$

This result seems to be in accord with the report that methyl chloride reacts in a melt of AlCl₃–NaCl with Al powder to give exclusively methylaluminum dichloride.[27] On the other hand,

as discussed with Al powder, methyl chloride gives methyl-aluminum sesquichloride.[26] Similarly, methyl iodide reacts with AlI₃ + Al.

Reduction of AlCl₃ with very active aluminum could also give AlCl, which then reacts under electrolysis conditions[28] to give ethylaluminum diiodide. Methyl iodide otherwise reacts with Al powder to give the sesquiiodide.[26]

There is a significant difference between the reaction of alkyl halides with aluminum yielding alkylaluminum sesquihalides and aluminum dihalides giving alkylaluminum dihalides.

We suggest that the reaction of alkyl halides with Al involves intermediate formation of alkylaluminum monochlorides (probably via a single electron-transfer process, as suggested by Ashby[29] for the formation of analogous Grignard reagents).

$$RX + Al^0 \rightarrow [R^{\bullet} + {}^{\bullet}AlX] \rightarrow RAlX$$

$$2RAlX \rightleftharpoons [R(X)Al]_2$$
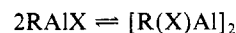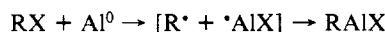
As the reaction proceeds in the absence of ether or other complexing agents, the alkylaluminum monohalides dimerize (through halogen bridging and Al–Al bonding) and then react with excess alkyl halide to give alkylaluminum sesquihalides.

$$2RX + 2Al \rightarrow (RAlCl)_2$$

$$[RAlCl]_2 + RCl \rightarrow R_2AlClRAlCl_2$$
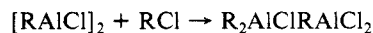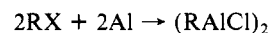
Alternatively, monomeric RAlCl itself (a radical) can react with alkyl halides.

$$RAlX + RX \longrightarrow RAlX_2 + {}^{\bullet}R \xrightarrow{RAlX} R_2AlX$$
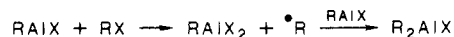
There is, however, a very limited amount of radical coupling product formed (i.e., R–R), which indicates that the latter pathway is less significant.

The reaction of pretreated AlCl₃ + Al (i.e., AlCl₂) with alkyl halide supports the related mechanism.

$$(AlX_2)_2 + RX \rightarrow RAlX_2 \cdot AlX_3$$

or

$$AlX_2 + RX \rightarrow RAlX_2 + X^{\bullet} \xrightarrow{AlX_2^{\bullet}} RAlX_2 \cdot AlX_3$$

The AlCl formed may also directly react with alkyl (or aryl) halides.

$$RCl + AlCl \rightarrow [R^{\bullet} + {}^{\bullet}AlCl_2] \rightarrow RAlCl_2$$
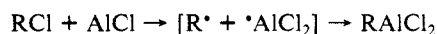
However, it is difficult to ascertain the presence of AlCl in the reaction mixture as it also reacts as discussed with AlCl₃ present to give AlCl₂.

When diethylaluminum chloride is reacted with potassium metal, triethylaluminum and aluminum metal are formed.

$$2(Et_2AlCl)_2 \xrightarrow[0\,°C]{3K} (AlEt_3)_2 + Al$$
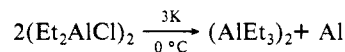
Aluminum powder reacts similarly with diethylaluminum chloride. These reactions are best explained by a radical mechanism through initial reduction to Al(Et)₂. No Al–Al-bonded dimer in this case could be observed,[19] contrasted with the bulkier isobutyl system.[6]

$$Et_2AlCl \rightarrow Et_2Al \xrightarrow{Et_2AlCl} Et_3Al + EtAlCl$$
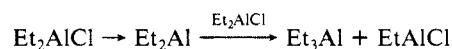
Pyridine is known to react with AlCl₃ to form an acid–base complex of the type **10**. This complex may be reduced, either through electrochemical means or through reducing metals (e.g. K) to give the corresponding free radical **11**.

(26) For review, see: (a) Grosse, A. V.; Mavity, J. M. *J. Org. Chem.* **1940**, *5*, 106. (b) Lehmkuhn, H.; Ziegler, K. In *Houben-Weyl Methoden der Organischen Chemie*, 4th ed.; Thieme: Stuttgart, FRG, 1970; Vol. 1314, pp 63–67, and references therein.
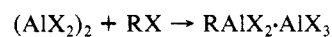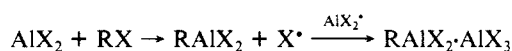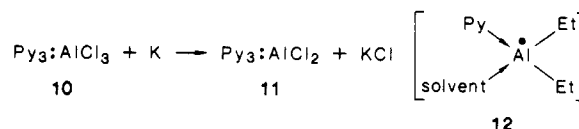
(27) Sundermeyer, W.; Verbeck, W. Ger. Offen. 1 239 687; *Chem. Abstr.* **1968**, *68*, 2989.

(28) Chadwick, J. R.; Kinsella, E. *J. Organomet. Chem.* **1965**, *4*, 334.

(29) Ashby, E. C. *Pure Appl. Chem.* **1980**, *52*, 545.

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Other Al(II) radicals involving aluminum alkyls are also known. The free radicals in the form of complexes such as **11** and **12** have been studied earlier by ESR.[30-32] $AlCl_3(g)$ and Al (580 °C) reacted as discussed previously to give $(AlCl_2)_2$, which reacts with pyridine to give a complex. This complex is ESR active (g = 2.0129), yet the spectrum is somewhat different from the reported monomeric $Py_3:AlCl_2$ spectrum (g = 2.0033, a_{Al} = 1.77 G). The difference is thought to reflect the associated nature of $(AlCl_2)_2$. The spectrum is consistent with that of associated $AlCl_2$ with active sites randomly spaced on the surface. The higher "g" value reflects an influence of the inner Cl atoms affecting the occupancy of the electron. The lack of hyperfine structure may reflect the presence of suspended particles in the sample.
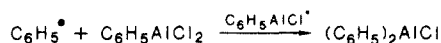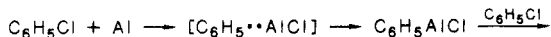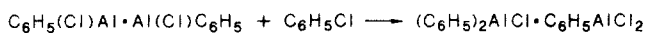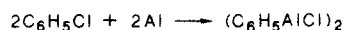
Iodo-, bromo-, and chlorobenzenes also react with $AlCl_3$ + Al to give phenylaluminum dihalides.

$$C_6H_5X \xrightarrow{2AlCl_3-Al} C_6H_5AlX_2$$
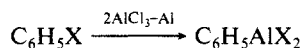
The reaction as depicted for chlorobenzene can proceed, as discussed previously for methyl chloride, through intermediacy of $(AlCl_2)_2$ or by a radical pathway.

$$C_6H_5Cl + (AlCl_2)_2 \rightarrow C_6H_5AlCl_2 + AlCl_3$$

$$C_6H_5Cl + AlCl_2{}^\bullet \rightarrow AlCl_3 + C_6H_5{}^\bullet \xrightarrow{AlCl_2{}^\bullet} C_6H_5AlCl_2$$
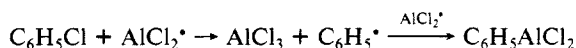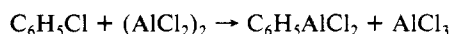
The reaction is again different from the known reaction of aluminum metal with chlorobenzene giving phenylaluminum sesquichloride, which, however, proceeds only with very active aluminum[33]

$$2C_6H_5Cl + 2Al \rightarrow (C_6H_5AlCl)_2$$

$$C_6H_5(Cl)Al\cdot Al(Cl)C_6H_5 + C_6H_5Cl \rightarrow (C_6H_5)_2AlCl\cdot C_6H_5AlCl_2$$

$$C_6H_5Cl + Al \rightarrow [C_6H_5{}^{\bullet\bullet}AlCl] \rightarrow C_6H_5AlCl \xrightarrow{C_6H_5Cl}$$

$$C_6H_5{}^\bullet + C_6H_5AlCl_2 \xrightarrow{C_6H_5AlCl{}^\bullet} (C_6H_5)_2AlCl$$

Biphenyl is a by-product of the reaction above 150 °C, clearly indicating dimerization of C_6H_5 radical at high temperatures.

Wittenberg[34] has attempted to increase the reactivity of aluminum metal by grinding it with $AlCl_3(AlBr_3)$. Other attempts involved aluminum–magnesium alloys. More recently Rieke[35] obtained highly activated aluminum powder by reducing anhydrous aluminum trihalides in organic solvents such as THF, xylene, and triethylamine under nitrogen atmosphere with potassium or sodium metal. This activated aluminum reacts completely with bromo- or iodobenzene in refluxing xylene in 5 min compared with several days of reflux needed by Grosse[26a] and hours by Wittenberg[34] with less reactive aluminum.

Rieke[35] uses a threefold molar excess of potassium or sodium to reduce $AlCl_3(AlBr_3)$.

$$AlCl_3 + 3M \rightarrow Al \text{ (activated)} + 3MCl \qquad M = K, Na, Li$$
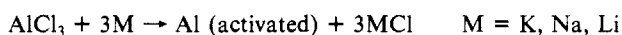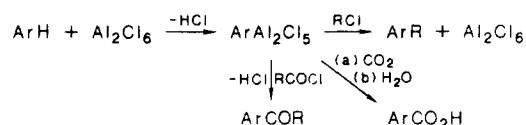
In contrast, in our work, reduction of $AlCl_3$ to $AlCl_2$ was generally carried out with a twofold molar excess of $AlCl_3$ ($AlCl_3$ to Al mole ratio of 2:1).

$$2AlCl_3 + Al \rightarrow 3AlCl_2$$

On the basis of the discussed chemistry, it is rather clear that the activity of metallic aluminum can vary depending on the reaction conditions as well as methods of preparation.[26b] We are not suggesting that the $2AlCl_3$ + Al composition gives pure $AlCl_2$. Similarly, it is also possible that in some preparations of activated aluminums some aluminum sub-halides may also be present.

In this regard it is interesting to note that more than 100 years ago Friedel and Crafts suggested that the reactions, which came to bear their name, proceed by way of organoaluminum compounds.[36] To account for aromatic alkylation, acylation, and even some observed carboxylation with CO_2, they suggested possible intermediate formation of arylaluminum dichloride (as its $AlCl_3$ complex).

$$ArH + Al_2Cl_6 \xrightarrow{-HCl} ArAl_2Cl_5 \xrightarrow{RCl} ArR + Al_2Cl_6$$

$$-HCl \Big| RCOCl \overset{(a) CO_2}{\underset{(b) H_2O}{\diagdown}}$$

$$ArCOR \qquad ArCO_2H$$

No evidence was obtained, however, since (including our studies) to substantiate that aluminum trichloride reacts with benzene to give phenylaluminum dichloride. It is now recognized that in Friedel–Crafts reactions anhydrous $AlCl_3$ activates the alkyl (acyl) halides by forming electrophilic complexes or carbocations with only weak interaction with the hydrocarbon substrates, although in the presence of protic coacids the conjugated strong Friedel–Crafts acids can protonate hydrocarbons. At the same time, however, it is by now impossible to establish the purity of aluminum trichloride used by Friedel and Crafts in their pioneering work. Presence of some metallic aluminum in the $AlCl_3$ employed could account for some of their results.

It is also interesting to point out that Friedel and Crafts discovered their alkylation reaction studying Wurtz–Zincke-type coupling of alkyl halides with aluminum turnings, activated by traces of iodine. During the course of these studies, they observed that after a longer initiation period the reaction mixture heats up and a complex mixture of products was formed. They eventually concluded that the reaction was due to the in situ formation of aluminum trichloride. Subsequently, they reacted benzene with alkyl halides in the presence of aluminum trichloride, and thus the Friedel–Crafts reaction was born. What was not discussed at the time or since is the question how aluminum trichloride is formed and what other intermediate products are involved in the system. On the basis of the results presented in this paper, it is indicated that the formation of $AlCl_3$ in the reaction of alkyl chlorides with aluminum metal in the pioneering work of Friedel and Crafts must have involved intermediate formation of alkyl-aluminum monochlorides and aluminum dichloride, respectively.

The reactions of aluminum dihalides are generally carried out in hydrocarbon solvents. Ethers, frequently used in organometallic chemistry as solvents, are unsuitable because they not only strongly complex with aluminum halides but also react with aluminum dihalides.

Illustrative is the reaction of dimethyl ether. When dimethyl ether is treated with $AlCl_3$ + Al at 120–140 °C, methylaluminum dichloride as well as methoxyaluminum dichloride is formed. Hydrolysis of the product mixture gave methane, hydrogen chloride, and methyl chloride.

$$3(CH_3)_2O + 4AlCl_3 + 2Al \rightarrow 3CH_3AlCl_2 + 3CH_3OAlCl_2$$
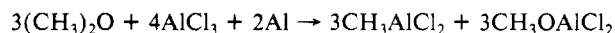
Aluminum trichloride itself under the reaction conditions does not react with dimethyl ether, except for complexation. There is also no evidence of protolytic cleavage of dimethyl ether. These observations indicate that it is the in situ formed aluminum dichloride that reacts with dimethyl ether.

$$CH_3OCH_3 + Cl_2AlAlCl_2 \rightarrow CH_3AlCl_2 + CH_3AlCl_2$$
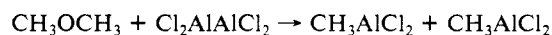
Conclusions

In conclusion, aluminum dihalides as well as alkyl(aryl)aluminum monohalides were found to play a significant role in the preparation of organoaluminum reagents. Aluminum dichloride

(30) Köster, R.; Benedikt, G.; Schrötter, H. W. *Angew. Chem.* **1964**, *76*, 649.

(31) Lehmkuhl, H.; Fuchs, G.; Koester, R. *Tetrahedron Lett.* **1965**, 2511.

(32) Ziegler, E.; Fuchs, G.; Lehmkuhl, H. *Z. Anorg. Allg. Chem.* **1967**, *355*, 145.

(33) Lehmkuhl, H.; Ziegler, K. In *Houben-Weyl Methoden der Organishen Chemie*, 4th ed.; Thieme: Stuttgart, FRG, 1970; Vol. 1314, pp 173–174, and references therein.

(34) Wittenberg, D. *Justus Liebigs Ann. Chem.* **1962**, *654*, 23.

(35) Rieke, R. D.; Chao, L. C. *Synth. React. Inorg. Met.-Org. Chem.* **1974**, *4*, 101.

(36) Friedel, C.; Crafts, J. M. *C.R. Hebd. Seances Acad. Sci.* **1877**, *85*, 74.

Aluminum Dichloride and Dibromide

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and dibromide were prepared and isolated for the first time by the reaction of aluminum metal with aluminum trihalides, tetraisobutyldialane with HCl, and Al atoms with Cl_2 using matrix isolation techniques. They were studied spectroscopically (by IR and Raman), and their reaction such as addition to olefins and reaction with alkyl (aryl) halides were investigated. Similarly, the reaction of alkyl (aryl) halides with reactive aluminum powder (turnings) or reduction of alkyl(aryl)aluminum dihalides with aluminum (or related reducing metals) gives alkyl(aryl)aluminum monohalides. The evolving chemistry of aluminum sub-halides and their alkyl (aryl) derivatives extends the scope and opens up interesting new aspects of organoaluminum chemistry.

Experimental Section

General Aspects. All reactions described in this investigation were extremely sensitive to oxygen and moisture and thus were carried out under pure argon on standard vacuum lines equipped with mercury float valves. All solvents and starting materials were carefully dried and degassed. Al powder (99.999%) and Al foil (99.999%) were purchased from Alfa. $AlCl_3$ (99.999%) was twice resublimed prior to use. Alkylaluminum chlorides were purchased from Aldrich Chemicals and were used as received. Gallium(III) chloride, diisobutylaluminum chloride and triisobutylaluminum chloride were obtained from Alfa Chemicals and were used as received. Cyclohexene (Aldrich Chemicals) was dried over P_2O_5 and distiled prior to use.

$Ga(GaCl_4)$ and $Ga(GaBr_4)$ were prepared according to the literature methods.[37]

^1H, ^2H, and ^{13}C NMR spectra were recorded on a Varian Associates Model XL-200 NMR spectrometer equipped with variable-temperature broad-band and $^1H/^{19}F$ fixed-frequency probes. ^{27}Al, ^{71}Ga, and ^{69}Ga NMR spectra were obtained on a Varian Associates Model FT-80 NMR spectrometer. IR spectra were recorded on an IBM Model 9000 IR/30S DTGS/CSF spectrometer. Matrix IR studies were carried out with a Nicolet 5 DXB FTIR spectrometer. GC–MS analysis was carried out on a Finnigan Mat Model 700 GC–MS equipped with an ion-trap detector and a Varian Associates Model 3500 gas chromatograph. ESR measurements were carried out on an IBM–Bruker spectrometer. X-ray powder diffraction was obtained on a Syntex P_{21} diffractometer using Mo $K\alpha$ radiation. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

General Procedure for the Reaction of Aluminum with Aluminum Trihalides. (a) Mixtures of $AlCl_3$ (10 g, 74 mmol) and Al (1.0 g, 37 mmol), $AlBr_3$ (19.73 g, 74 mmol) and Al (1.0 g, 37 mmol), $AlCl_3$ (10 g, 74 mmol) and K (1.45 g, 37 mmol), or $AlBr_3$ (19.73 g, 74 mmol) and K (1.45 g, 37 mmol) were heated in a 200-mL Monel autoclave under argon atmosphere at 120 °C for 5–10 h. The autoclave was then cooled and degassed, and the gray-black materials were removed in argon atmosphere. They were used as specified for each reaction. (b) A mixture of reducing metal and aluminum trihalide as under (a) was, in methylcyclohexane, first subjected to ultrasound treatment for 3 h in a Schlenk flask using an ultrasonic bath and heated subsequently under reflux or reacted at 120 °C in an autoclave for 5–10 h as under (a).

Preparation of Aluminum Dihalide at High Temperature in a High-Vacuum System. A mixture of $AlCl_3$ (0.65 g, 4.84 mmol) and Al foil (0.07 g, 2.7 mmol) was sealed under vacuum (4 × 10^{-7} Torr) in a thick-walled quartz tube. The system was heated to 580 °C for 20 h in a Lindberg Type 55035 furnace. After cooling, the quartz tube was transferred to an inert-atmosphere drybox. The light gray material isolated from the quartz tube under argon atmosphere was subjected to IR spectroscopic analyses.

Reaction of Al Atoms with Cl_2. A mixture of Cl_2 and Ar in mole ratios between 1:60 and 1:240 was codeposited with aluminum atoms evaporated from a solid aluminum metal sample, either (i) out of an alumina furnace or (ii) out of a heated tungsten spiral wire embracing the sample (tungsten basket), onto a 12 K CsI window. Aluminum atom concentration was controlled by the current heating the aluminum furnace or the tungsten basket. Accurate temperature measurement was not possible, but the temperature was 1050 ± 50 °C on the basis of the color for each method. The tungsten basket was especially suited for longer deposition periods (up to 7 h) due to the lower heat load since the aluminum sample was in direct contact with the heater wire. Standard matrix deposition techniques were employed.[38,39] Spectra were recorded on a Nicolet 5 DXB FTIR spectrometer using 2-cm^{-1} resolution, and band positions are accurate to better than 0.5 cm^{-1}. Spectra in absor-

bance mode were background corrected.

Reaction of Pyridine with Aluminum Dihalide (High Temperature). The product from the high-temperature reaction of Al + $AlCl_3$ (50 mg) was stirred in 3 mL of dry degassed pyridine for 30 min and then dried in vacuo. This material was then treated with 10 mL of THF. The supernatant was characterized by ESR spectroscopy; $g = 2.0129$, $W = 34$ G.

X-ray Powder Diffraction Studies of Aluminum Halides. Samples of Al_2Cl_6 and $AlCl_2$ from the Al + $AlCl_3$ reactions (high temperature) and $Al_2(i\text{-Bu})_{4-x}Cl_x$ were packed into 0.7-mm capillary tubes and sealed under a N_2 atmosphere. Data were collected with a step size of 0.1 2θ/point, with a scan rate of 1.5 2θ/min and 2θ values ranging from 5 to 50° using Mo $K\alpha$ (0.710 69) radiation.

Reaction of Ethylene with Aluminum and Aluminum Trichloride. A 200-mL Monel autoclave equipped with a mechanical stirrer was charged with aluminum (1.0 g, 37 mmol), aluminum trichloride (2.1 g, 15 mmol), and methylcyclohexane (25 mL) under argon atmosphere. The autoclave was then charged with 3 atm of ethylene and stirred for 12 h at 90–95 °C. The dark red reaction product was transferred into a flask and filtered under argon. The filtrate was treated with 25 mL of n-pentane to precipitate **9** as a beige solid. The solvent containing ethylaluminum chlorides was removed by filtration, and the solid product was washed several times with n-pentane to remove any residual ethylaluminum halides. After solvent was removed in vacuo at 50 °C, 2 g of 1,1-bis-(dihaloaluminio)ethane **9** was obtained. ^1H NMR: δ -0.6 (q, $J_{H-H} = 7$ Hz), 1.52 (d, $J_{H-H} = 7$ Hz). ^{13}C NMR: δ -1.9 (d), 10.0 (q). ^{27}Al NMR: δ -23 (br).

(a) Deuteriolysis of 9. In an argon atmosphere, 1 g of **9** in 25 mL of methylcyclohexane was deuteriolyzed with 5 mL of D_2O. The gaseous product was collected and analyzed by GC–MS, showing 95% ethane-$1,1$-d_2.

(b) Carboxylation of 9 was effected by heating it in methylcyclohexane at 80 °C under 75 atm of CO_2 followed by usual workup. Methylmalonic acid was obtained, which was found to be identical with an authentic sample.

(c) Mercuration was effected by stirring equimolar amounts of **9** and mercuric chloride in tetrahydrofuran at 25 °C. Obtained 1,1-bis(chloromercurio)ethane was found to be identical with that reported.[40]

(d) Reaction of 9 with HCl. Dry hydrochloric acid was passed into a solution of **9** (1 g in 25 mL of methylcyclohexane) and stirred for 1 h. Analysis of the gases showed formation of 97% ethane. The analysis of liquid product by ^1H, ^{13}C, and ^{27}Al NMR spectroscopy, after removal of methylcyclohexane, showed the presence of ethylaluminum dichloride.

Reaction of Cyclohexene with Aluminum and Aluminum Trihalides. To prereacted aluminum (0.2 g, 7 mmol) and aluminum trichloride or tribromide (15 mmol), respectively, (in 20 mL of methylcyclohexane) was added cyclohexene (1.53 g, 18.7 mmol) at 0 °C. The mixture was heated for about 5 h at 80 °C. The formed dark brown slurry was then deuteriolized with D_2O. The products were extracted in CH_2Cl_2 and dried over magnesium sulfate. Analysis by GC–MS showed 4% cyclohexane-$1,2$-d_2.

The reaction of aluminum trichloride and aluminum metal under sonication following the above procedures also led to 14% cyclohexane-$1,2$-d_2.

Reaction of Aluminum Dichloride with Aluminum and Aluminum Trichloride. A 200-mL Monel autoclave containing prereacted Al + $AlCl_3$ equivalent to 11 g (0.11 mol) of $(AlCl_2)_2$ was charged with 35 atm methyl chloride and heated to 120 °C for 18 h. The autoclave was then cooled, unreacted methyl chloride was degassed, and the remaining product was identified (IR, NMR) as methylaluminum dichloride. When further reacted with CO_2 (75 atm) by heating to 100 °C for 12 h, the resulting mixture upon hydrolysis with $H_2O/NaOH$ (10:1) workup gave sodium acetate.

Reaction of Dialkylaluminum Halides with Potassium or Aluminum. In a glass-jacketed reaction tube connected to an argon line and equipped with a cooling circulator (ethylene glycol/water (1:1)), diethylaluminum chloride (3.0 g, 31 mmol) and potassium (1 g, 25 mmol) or aluminum (0.75 g, 27 mmol) in 25 mL of hexane were reacted for 5 days at 0 °C upon which a precipitate was formed. After filtration and removal of solvent, triethylaluminum was obtained, identified by ^{13}C NMR. ^{13}C NMR: 12 (C_1); 8.17 (C_2). ^{13}C NMR (diethylaluminum chloride): δ 2.52 (C_1) and 7.04 (C_2).

Reaction of Cyclohexene with $AlCl_2$ (Low Temperature). To 20 mg of $AlCl_2$ (prepared from tetraisobutyldialane) was added 3 mL of dry degassed cyclohexene, and the resulting solution was stirred for 10 min. To this mixture was added 1 mL of D_2O (degassed) with Schlenk techniques. The organic phase was extracted with 10 mL of Et_2O and dried over $MgSO_4$. The liquid was analyzed by GC–MS showing 35% 1,2-

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dideuteriocyclohexane (based on $AlCl_2$).

Reaction of Bromobenzene with Aluminum and Aluminum Trichloride.
Bromobenzene (22 mmol) was added to a slurry of aluminum dichloride (74 mmol obtained by $AlCl_3$ + K) in xylene. After the solution was stirred for 10 h at 100 °C, the solvent was removed by vacuum and the slurry was quenched with 10% HCl. The GC analysis of the products showed benzene (55%) and unreacted bromobenzene (40%).

Reaction of Dimethyl Ether with Aluminum and Aluminum Trichloride.
Into a 200-mL Monel autoclave was charged the reaction product of aluminum trichloride (110 mmol) and aluminum (60 mmol) in 30 mL of xylene under argon. A total of 10 mL of dimethyl ether was then added at -30 °C; the vessel was closed and heated from 70 to 190 °C for 3 h. The autoclave was then cooled, and the product (obtained by hydrolysis) was analyzed by GC-MS showing methane (31%), methyl chloride (29%), and unreacted dimethyl ether (39%) with traces of ethane

and butane.

4-Oxazoline Route to Stabilized Azomethine Ylides.
Controlled Reduction of Oxazolium Salts

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Abstract: Treatment of oxazolium salts with phenylsilane/CsF generates 4-oxazolines **14** in situ. Provided that R_4 = H or alkoxy, ring opening to azomethine ylides **15** occurs spontaneously and [2 + 3] cycloadducts are obtained in the presence of acrylate, *N*-phenylmaleimide, propiolate, or dimethyl acetylenedicarboxylate (DMAD) dipolarophiles. If R_5 = alkyl or aryl, the initially formed 4-oxazoline resists ring opening, probably due to steric interactions in the dipole, and affords products **30** derived from 2 + 2 trapping with DMAD. In typical cases, the [2 + 3] cycloadducts are formed with geometry corresponding to the trapping of the S-dipole **15** to the exclusion of other dipole isomers. Pyrolysis of analogous *N*-methylaziridines results in an equilibrated dipole, although the major adduct also corresponds to the trapping of **15**. Dipole trapping with phenyl vinyl sulfone is also possible, and reductive desulfonylation with sodium amalgam affords the adduct **41**, which corresponds to the adduct of the stabilized azomethine ylide with ethylene. Overall, the oxazolium salt reduction provides access to a large variety of azomethine ylides stabilized by acyl, ester, benzoyl, and formyl substituents. The dipoles can be generated and trapped at room temperature or below.

Azomethine ylides have been extensively studied since the 1965 discovery that they can be generated by pyrolysis of aziridines. The reaction of 1,2,3-triphenylaziridine with electron-deficient olefins or acetylenes to yield five-membered nitrogen rings was reported by Heine and Peavey,[1a] and similar independent findings were described by Padwa and Hamilton[1b] and by Huisgen, Scheer, Szeimies, and Huber.[1c] Due to the systematic investigations by Huisgen et al., it is now well known that thermolysis of 1-phenyl-2,3-dicarbomethoxyaziridine involves conrotatory ring opening to the carbonyl-stabilized ylides **3** or **4**.[2] Trapping products of the S-dipole **3** are obtained from the cis aziridine **1**, while adducts of the isomeric W-dipole **4** result from the trans aziridine **2**. The S-dipole **3** is trapped by several dipolarophiles without loss of dipole geometry. In contrast, the W-dipole **4** reacts cleanly only with the most reactive of traps such as dimethyl acetylenedicarboxylate (DMAD). With less reactive dipolarophiles (fumarate and norbornene), products derived from the S-dipole **3** are also observed due to dipole interconversion. These topics have been extensively reviewed, and the concepts have been extended to nonstabilized azomethine ylides.[3-9]

Many other examples of aziridine thermolysis have been reported in the literature.[10-18] The mechanism of dipole trapping

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