in the vacuum system upon warming to −20 °C. An indication of the difficulties involved in these syntheses is that 54 separate attempts were required to produce the data presented here.

Numerous attempts to prepare $Ba^{2+}C222\cdot(Na^-)_2$ over a time span of 6 years by three different investigators in our laboratory have failed to yield conclusive results. While bronze precipitates can be formed, the analyses are poor, decomposition products are obviously present, and crystals of $Na^+C222\cdot Na^-$ are present in the precipitate.

It is clear that the easiest crystals to prepare and the most stable are sodides. This is probably because of the stability of Na^- to dissociation into Na^+ and trapped electrons. While no experimental data are available for the thermodynamics of this dissociation in solids, estimates of the equilibrium constants for eq 3 in ethylenediamine[8] are revealing. We

$$M^- \rightleftharpoons M^+ + 2e^-_{solv} \qquad (3)$$

expect Na^+ to be stabilized more than K^+, Rb^+, or Cs^+ in this solvent. In spite of this, the dissociation constant, K_3, for Na^- is about 5, 4, and 6 orders of magnitude *smaller* than for K^-, Rb^-, and Cs^-, respectively. The much lower stability of electrides than alkalides suggests that the formation of trapped electrons by dissociation of M^- would greatly decrease the stability of the solid alkalide salt. For this reason also, coprecipitation of alkalides and electrides would lead to lower stability. Finally, both electrides and sodides appear to be more stable when 18-crown-6 is used as the complexing agent instead of a cryptand. For example, crystals of $Cs^+18C6\cdot Na^-$ did not change in appearance when allowed to remain at room temperature for 1 week, whereas crystals of $Cs^+C222\cdot Na^-$ decomposed rapidly above −20 °C.

An analysis problem which is particularly troublesome with the more reactive alkalides, especially with salts of K^-, Rb^-, and Cs^- occurred during the hydrogen evolution step. Reaction with water which was condensed from the vapor onto the salt caused some decomposition of the cryptand without hydrogen evolution. When this occurred, the residue was straw colored and the subsequent ^1H NMR analysis showed that (unidentified) decomposition products of the cryptand were formed. This is believed to be the cause of low analyses for H_2 in many cases. For example, a sample of $Rb^+C222\cdot Rb^-$ (5×10^{-5} mol) which contained only shiny, bronze crystals before reaction with water, formed a dark residue upon reaction with water at about −20 °C. Only 19% of the expected H_2 was formed, and, while the pH titrations and flame analyses were satisfactory, the ^1H NMR spectrum showed substantial amounts of cryptand decomposition products. These products were not identified, but the complex ^1H NMR spectra show that the cryptand was altered. The autocatalytic nature of alkalide decomposition reactions suggests that free radical formation probably occurs which could lead to oligomerization of the cryptand. Attempts to decrease the extent of decomposition during the hydrogen evolution step by maintaining lower temperatures were not successful probably because ice formation occurred rather than direct reaction of water with the crystalline alkalide. Especially to be avoided is the addition of small amounts of *liquid* water to the crystalline sample since this results in excessive decomposition of the complexant.

This work shows that, except for salts of Li^-, it is possible to prepare crystalline salts of all alkali-metal anions. However, so far only certain salts containing Na^- are stable at room temperatures for extended periods of time. The most stable of these are $Na^+C222\cdot Na^-$, $Li^+C211\cdot Na^-$, $Cs^+18C6\cdot Na^-$, and $Cs^+C322\cdot Na^-$. It is especially encouraging that a stable salt of Na^- can be synthesized by using the relatively inexpensive crown ether 18-crown-6 since this should permit the preparation of bulk samples at moderate cost. The determination of the crystal structure of $Cs^+18C6\cdot Na^-$ is in progress.

Acknowledgment. This research was supported by NSF Grant DMR-79-21479. Much of the groundwork for these syntheses was done by Michael Yemen, Michael DaGue, and Harlan Lewis, and we gratefully acknowledge their contributions. The first preparation of crystalline $K^+C222\cdot K^-$ was done while J.L.D. was a John Simon Guggenheim Fellow and Fulbright Research Scholar with Professor J.-M. Lehn in Strasbourg, France. His assistance is gratefully acknowledged. We wish also to thank James Anderson and Holly Lystad, who worked on some aspects of this problem as undergraduate research assistants.

Registry No. $Cs^+C322\cdot Na^-$, 32611-46-4; $Rb^+C222\cdot Na^-$, 32611-96-4; $Na^+C221\cdot Na^-$, 80737-30-0; $K^+C222\cdot Na^-$, 66446-73-9; $Cs^+18C6\cdot Na^-$, 80737-31-1; $Rb^+C222\cdot Rb^-$, 57450-09-6; $Li^+C211\cdot Na^-$, 80737-32-2; $K^+18C6\cdot Na^-$, 80737-33-3; $K^+C222\cdot K^-$, 80737-34-4; $Cs^+C222\cdot Cs^-$, 57450-10-9; $Cs^+C222\cdot Na^-$, 80720-90-7.

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Attempted Syntheses of Low-Oxidation-State Organometallic Derivatives of Aluminum, Gallium, and Indium. A New Synthesis of $Al(CH_2SiMe_3)_3$

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The synthesis of $KAl(CH_2SiMe_3)_2$ by a reductive-elmination reaction between $Al(CH_2SiMe_3)_3$ and KH has been attempted, but a pure product could not be isolated. The reactants combine at 70 °C to form $KAl(CH_2SiMe_3)_3H$, a white pyrophoric solid, which has been fully characterized. A molecular weight study indicates the presence of a mixture of monomeric and dimeric species in benzene solution. The pyrolysis of $KAl(CH_2SiMe_3)_3H$ at 205 °C produces $Si(CH_3)_4$ but also CH_4. The formation of $Si(CH_3)_4$ suggests that $KAl(CH_2SiMe_3)_2$ might have been formed, but the presence of CH_4 indicates that a decomposition reaction occurs either prior to or after the formation of $KAl(CH_2SiMe_3)_2$. The reactions of mixtures of $KH–Al(CH_3)_3$, $KH–Ga(CH_3)_3$, $NaH–Ga(CH_3)_3$, $KH–In(CH_3)_3$, and $NaH–In(CH_3)_3$ have also been investigated in order to determine the role of the organic substituent in the attempted reductive-elimination reactions. In all cases the formation of CH_4 during pyrolysis of $KAl(CH_3)H$, $KGa(CH_3)_3H$, and the other reaction mixtures is consistent with the occurrence of reduction, but no pure compounds could be isolated. A new synthetic route to $Al(CH_2SiMe_3)_3$ from $AlBr_3$ and $LiCH_2SiMe_3$ in refluxing hexane is also described.

Introduction

An interesting new area of research activity centers on the chemistry of the organometallic derivatives of main-group metals in their low oxidation states. In group 3 chemistry the list of low-oxidation-state compounds that are thermally stable at room temperature is very limited but includes KGa-

$(CH_2SiMe_3)_2$,[1] $NaIn(CH_2SiMe_3)_2$,[2] $In(C_5H_5)$,[3,4] $In(C_5H_4CH_3)$,[4] and $Tl(C_5H_5)$.[5] The cyclopentadienylindium and -thallium compounds have been known for many years. In contrast the gallium(I) and indium(I) (trimethylsilyl)methyl derivatives are new compounds, which are prepared by a novel reduction reaction (eq 1). All data[1,2] are consistent with the

$$Ga(CH_2SiMe_3)_3 + KH \xrightarrow[\text{elimination}]{\text{reductive}} KGa(CH_2SiMe_3)_2 + SiMe_4 \quad (1)$$

hypothesis that the preparative reaction involves a reductive-elimination reaction of a hydride intermediate, $K[Ga(CH_2SiMe_3)_3H]$ or $Na[In(CH_2SiMe_3)_3H]$. The synthetic procedures for the reactions are experimentally attractive, require mild conditions (30–50 °C in benzene), and lead to the quantitative formation of products.

One goal of our research program is to determine whether the apparent reductive-elimination reaction is a general route to low-oxidation-state, main-group organometallic compounds. The potential variables in the reaction scheme are the central main-group atom, the alkali-metal hydride, and the organic substituent. The initial investigation of the reduction of $In(CH_2SiMe_3)_3$ with an alkali-metal hydride indicated that the desired reaction occurred very readily.[1] Similarly, the gallium(III) derivative[2] was converted to the gallium(I) anion without any difficulty or unusual conditions. Our research had also indicated that the specific alkali-metal hydride influenced the ease of the reaction. Of the hydrides studied, KH was more reactive than NaH or LiH. The obvious direction of our research was to extend the reduction reaction to aluminum chemistry. Consequently, we have studied the reaction of $Al(CH_2SiMe_3)_3$ with KH to determine whether $KAl(CH_2SiMe_3)_2$ could be synthesized. We also wanted to determine whether the organic substituent played an active role in determining the relative ease of the reductive-elimination reaction. Therefore, we investigated the potential of reaction mixtures of $In(CH_3)_3$, $Ga(CH_3)_3$, and $Al(CH_3)_3$ with alkali-metal hydrides to undergo the reductive-elimination reaction.

Experimental Section

All compounds described in the investigation were extremely oxygen and moisture sensitive and were manipulated in a vacuum line or a purified argon atmosphere. The solvents were purified by refluxing with an appropriate drying agent and vacuum distilled just prior to use. Lithium metal and the alkali-metal hydrides were purchased from Alfa Inorganics as oil dispersions. The oil was removed by repeated extractions with dry pentane or hexane. ((Trimethylsilyl)methyl)lithium,[6] $LiCH_2SiMe_3$, was prepared from Me_3SiCH_2Cl and Li in either diethyl ether or hexane and purified by sublimation at 90 °C. Trimethylgallium, $Ga(CH_3)_3$, was purchased from Alfa Inorganics. Trimethylindium, $In(CH_3)_3$, was prepared from InI_3 and CH_3MgI in diethyl ether and purified.[7] Methane and hydrogen formed in pyrolysis reactions were measured with a Toepler pump and gas buret assembly.

Characterization Methods. New compounds were analyzed for their group 3 metal content, bound organic substituents, and hydrogen. The group 3 metals were determined by EDTA titration.[8] The bound organic ligand and the hydride ligand were converted to the corresponding alkane or H_2 by acid hydrolysis, purified, and quantitatively measured by mass or volume measurements. Molecular weight measurements were obtained cryoscopically in benzene by using an instrument similar to that described by Shriver.[9] The infrared spectra were recorded in the range 4000–250 cm^{-1} by means of a Perkin-Elmer Model 457 spectrometer. The spectra were recorded as Nujol mulls by using CsI plates. Bands due to mulling agents have been omitted. The ^{1}H NMR spectra were recorded at 90 MHz and ambient temperature by using a Varian EM-390 spectrometer. All chemical shifts (τ) are referenced to tetramethylsilane as 10.00 ppm.

Synthesis of $Al(CH_2SiMe_3)_3$. Tris((trimethylsilyl)methyl)aluminum, $Al(CH_2SiMe_3)_3$, was prepared from $AlBr_3$ and $LiCH_2SiMe_3$ in hexane. In the drybox, 6.74 g (71.7 mmol) of $LiCH_2SiMe_3$ and 70 mL of hexane were combined in an addition funnel equipped with a high-vacuum Teflon valve and a stirring bar. Hexane (100 mL) was distilled into a three-neck 250-mL flask equipped with a stirring bar and charged with 6.39 g (23.9 mmol) of $AlBr_3$. A reflux condenser and the addition funnel were placed on the flask under a flow of argon. The stirring bar in the dropping funnel was agitated to insure complete dissolution of $LiCH_2SiMe_3$ in hexane, and then this solution was slowly added to the stirred $AlBr_3$ suspension. An exothermic reaction immediately took place, precipitating LiBr. The reaction mixture was refluxed for 12 h, and then the solvent was removed by vacuum distillation. In the drybox the reaction flask was connected to a two-necked flask by a "90° tube". With use of an oil bath at 70 °C, 5.885 g (20.4 mmol) of $Al(CH_2SiMe_3)_3$ (85.4% yield) was distilled from the reaction vessel under high vacuum and collected in the two-necked flask; bp 48–49 °C (0.01 mm) (lit.[6] 51 °C/(0.08 mm)). ^{1}H NMR (CH_2Cl_2): τ 9.93 (CH_3), 10.24 (CH_2). IR (Nujol solution, cm^{-1}): 1265 (m, sh), 1253 (vs), 958 (s), 925 (s), 860 (vs), 832 (vs), 764 (vs), 736 (s), 690 (m), 662 (m), 590 (m).

Synthesis of $KAl(CH_2SiMe_3)_3H$. The compound, $KAl(CH_2SiMe_3)_3H$, was prepared by the reaction of $Al(CH_2SiMe_3)_3$ and KH. The reagents $Al(CH_2SiMe_3)_3$ (1.08 g, 3.74 mmol) and KH (0.17 g, 4.24 mmol) were combined in a break-seal tube equipped with a stirrer. Toluene (10 mL) was added by vacuum distillation; the tube was sealed at −196 °C and then heated at 70 °C for 24 h. The extent of reaction was monitored by observing the amount of insoluble KH. At the end of the reaction most of the solid KH had disappeared. The reaction tube was opened, the reaction mixture was filtered by means of a medium frit, the solvent was removed by vacuum distillation, and 1.11 g (3.37 mmol, 90.2% yield) of crude $KAl(CH_2SiMe_3)_3H$ (mp 138–141 °C) was isolated as a white solid. Traces of unreacted $Al(CH_2SiMe_3)_3$ were removed by washing the product with a small quantity of hexane at −20 °C. The melting point for $KAl(CH_2SiMe_3)_3H$ is 144–146 °C, and it decomposes at 205 °C. Anal. Calcd.: Al, 8.12; H, 1.00 mol/mol of Al; $SiMe_4$, 3 mol/mol of Al. Found: Al, 8.19; H, 0.99 mol/mol of Al; $SiMe_4$, 2.94 mol/mol of Al. ^{1}H NMR (benzene): τ 9.59 (s) (CH_3), 10.98 (s) (CH_2). IR (Nujol mull, cm^{-1}): 1560 (w, br), 1250 (s), 1161 (w), 1024 (m), 944 (s), 920 (s), 861 (vs), 839 (vs), 761 (s), 736 (s), 684 (m), 564 (m). Cryoscopic molecular weight (formula weight 328.7) (molality, observed molecular weight, association): 0.0874, 585, 1.78; 0.0556, 526, 1.60; 0.0436, 503, 1.53; 0.0290, 421, 1.28. The compound is soluble in ethers and aromatic hydrocarbons and moderately soluble in aliphatic hydrocarbons.

Synthesis of $KGa(CH_3)_3H$. The compound, $KGa(CH_3)_3H$, was prepared by the reaction of $Ga(CH_3)_3$ and KH in dimethoxyethane or benzene. The reagents $Ga(CH_3)_3$ (1.00 g, 8.74 mmol) and KH (1.05 g, 26.22 mmol) were combined in a break-seal tube. Dimethoxyethane (25 mL) was added by vacuum distillation. After 96 h at room temperature, the reaction mixture was filtered and the solvent was removed to leave $KGa(CH_3)_3H$ (1.250 g, 8.08 mmol), 92.5% yield); mp 150–152 °C. Anal. Calcd: Ga, 45.04. Found: Ga, 45.16. ^{1}H NMR (dimethoxyethane): τ 10.87, 10.93 (widths at half-height are 4 and 6 Hz, respectively). IR (Nujol mull, cm^{-1}): 2292 (m), 1254 (m), 1200 (m), 1161 (s), 1085 (s), 1030 (m), 990 (w), 847 (vs), 827 (vs), 700 (s), 577 (m), 555 (m), 512 (vs), 482 (vs).

Results and Discussion

The organoaluminum compound $Al(CH_2SiMe_3)_3$, the starting reagent for our attempted synthesis of an aluminum(I) species, has been previously reported.[10] However, it was prepared by a tedious reaction procedure. A 14-day reflux

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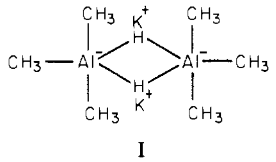
period for a mixture of $Hg(CH_2SiMe_3)_2$, Al foil, and toluene was required. Consequently, a more convenient route to $Al(CH_2SiMe_3)_3$ that avoided the long reaction time and the toxicity of the organomercury compound was developed. The two other common routes to organo group 3 compounds use Grignard reagents and lithium alkyls. The analogous gallium[1] and indium[2] compounds have been synthesized by the reaction of the Grignard reagent Me_3SiCH_2MgCl with $GaCl_3$ or InI_3 in diethyl ether. The reaction of the Grignard reagent with $AlCl_3$ produces the etherate $(Me_3SiCH_2)_3AlO(C_2H_5)_2$, a consequence of the high Lewis acidity of aluminum.[11] Therefore, a high-yield synthesis of $Al(CH_2SiMe_3)_3$ from $LiCH_2SiMe_3$[6] and $AlBr_3$ in hexane was developed. When the reaction mixture was refluxed for 12 h, $Al(CH_2SiMe_3)_3$ was isolated by vacuum distillation in 85% yield. If the reaction mixture was not refluxed, the organoaluminum product contained halogen atoms. It is of interest to note that the bulky (trimethylsilyl)methyl substituent leads to increased hydrolytic stability of $Al(CH_2SiMe_3)_3$ when compared to that of $Al(CH_3)_3$ and $Al(C_2H_5)_3$.

The synthesis of an aluminum compound in a formal low oxidation state has been attempted but without complete success. No pure, well-characterized organoaluminum(I) compound could be isolated. The research plan was to combine $Al(CH_2SiMe_3)_3$ with KH in a hydrocarbon solvent and to elevate the temperature. The formation of $Si(CH_3)_4$ would be consistent with the occurrence of a reductive-elimination reaction analogous to that observed in gallium[1] and indium[2] chemistry (eq 1). We had every reason to believe that the desired reductive-elimination reaction would occur. The literature even had an example of a reductive-elimination reaction in aluminum chemistry.[12] The thermal decomposition of $LiAlH_4$ at 187–218 °C has been reported to produce $LiAlH_2$ and H_2. However, our experimental data suggest that $KAl(CH_2SiMe_3)_2$ is not the final product because extensive decomposition involving the (trimethylsilyl)methyl substituent also occurs.

The reaction of $Al(CH_2SiMe_3)_3$ and KH in toluene at 70 °C gave $KAl(CH_2SiMe_3)_3H$, the apparent intermediate for the reductive-elimination reaction, in very high yield. This presumably "ionic" compound exists at room temperature as a colorless, pyrophoric solid and has considerable solubility in hydrocarbon solvents. Cryoscopic molecular weight studies in benzene suggest that $KAl(CH_2SiMe_3)_3H$ exists in solution as a mixture of monomeric and dimeric species. The apparent association in benzene varies from 1.28 to 1.78 in the concentration range of 0.029–0.087 M. A dimeric structure that involves hydride bridges and five-coordinate aluminum would be consistent with the observed association.



I

The infrared spectrum of $KAl(CH_2SiMe_3)_3H$ as a Nujol mull supports the proposed structure. There is a broad band at 1560 cm^{-1}, which is assigned to the aluminum–hydrogen stretching motion. The ^1H NMR spectrum is not helpful in learning more about the solution structure of $KAl(CH_2SiMe_3)_3H$, but it is reported in the Experimental Section.

When $KAl_2(CH_2SiMe_3)_3H$ was heated, melting occurred at 144–146 °C, but decomposition does not begin until 205 °C as shown by bubbling and formation of an off-white solid. The stoichiometry of the reaction reveals that 1 mol of $KAl(CH_2SiMe_3)_3H$ forms 1.53 mol of $Si(CH_3)_4$, 0.50 mol of CH_4, and an air-sensitive, fluffy white solid, which is insoluble in all nonreactive solvents including hydrocarbons and ethers. The properties of the solid prevented further identification. No data could be used to confirm the formation of $KAl(CH_2SiMe_3)_2$. The pyrolysis product has no infrared bands characteristic of an Al–H bond. The formation of 1 mol of $Si(CH_3)_4$ would be consistent with the proposed reductive-elimination reaction (eq 1). However, formation of CH_4 and the extra 0.53 mol of $Si(CH_3)_4$/mol of $KAl(CH_2SiMe_3)_3H$ suggests that the ligand has been involved in some type of decomposition reaction. There are no data that can be used to determine whether the proposed decomposition occurs prior to or after the formation of $KAl(CH_2SiMe_3)_2$.

The observed decomposition of the (trimethylsilyl)methyl groups and our goal to determine the role of the organic substituent in the reductive-elimination reaction prompted us to study the thermal reactions of $KAl(CH_3)_3H$. This compound was prepared by the method of Zakharkin and Gavrilenko.[13] The colorless compound does not melt but begins to decompose at 200 °C. After 4–5 h at this temperature, gas evolution appears to stop and 0.933 mol of CH_4/mol of $KAl(CH_3)_3H$ is formed. The product, a highly air-sensitive gray solid, is insoluble in hydrocarbon and ether solvents. Consequently, further identification of the material was difficult. The nearly stoichiometric evolution of methane could be consistent with the formation of an aluminum(I) compound by the reductive-elimination reaction, but other reactions are also possible. The gray color of the product suggests that some reduction to metallic aluminum occurs also. The insoluble nature of the solid could be consistent with an α-hydride elimination reaction. The thermal decomposition[14] of $Al(CH_3)_3$ at 298 °C yields methane and small quantities of ethane, ethylene, and hydrogen by apparent α-hydride reactions. The hydrolysis of the gray solid from thermal decomposition of 1 mmol of $KAl(CH_3)_3H$ produces 2.58 mmol of a gas that is principally CH_4 but also contains small amounts of H_2. The predicted hydrolysis products, if only $KAl(CH_3)_2$ had been present, would be 2 mol of CH_4 plus 1 mol of H_2. The thermal decomposition of 1 mmol of $KAl(CH_3)_3H$ at higher temperatures, 200–230 °C, for 12 h produced 1.18 mmol of a gas mixture consisting largely of CH_4 with also a small quantity of H_2. Thus, the thermal decomposition reactions of organoaluminum(III) hydrides are complex and do not lead to the quantitative formation of an aluminum(I) species.

The possible reactions of $Ga(CH_3)_3$ with alkali-metal hydrides have also been investigated. Trimethylgallium reacts with KH in dimethoxyethane or benzene at 25 °C to form $KGa(CH_3)_3H$, a colorless solid (mp 150–152 °C). The characteristic Ga–H stretching frequency is a sharp band at 2292 cm^{-1}. Since spectroscopic data confirmed the existence of a gallium hydride and no CH_4 was generated in the preparative reaction, the proposed reductive elimination did not occur at 25 °C. When a sample of $KGa(CH_3)_3H$ was heated at 110 °C for 72 h, no CH_4 or other evidence of reaction was observed. However, more extensive heating at 160 °C led to the formation of CH_4. After 72 h, 0.984 mmol of CH_4/mmol of $KGa(CH_3)_3H$ was formed. Heating for another 6 days produced an additional 0.506 mmol of CH_4/mmol of $KGa(CH_3)_3H$. The solid remaining in the pyrolysis tube had a gray-black color, and a "silver"-colored mirror of gallium metal coated the walls of the tube. The gray solid did not have any Ga–H bonds, according to its infrared spectrum. All of these results suggest that a well-defined product is not formed by

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a simple reductive-elimination reaction.

The reaction of NaH with $Ga(CH_3)_3$ was investigated in order to study the effects of the apparent reducing agent. Results that were different from those observed for KH were obtained. When 1 mmol quantities of both $Ga(CH_3)_3$ and NaH were combined in dimethoxyethane at 25 °C, 0.385 mmol of CH_4 was formed in 4 days. After the solvent was removed, the resultant mixture was heated at 135 °C for 72 h and an additional 0.216 mmol of CH_4 was formed. Further heating produced more CH_4; 145 °C for 72 h gave 0.124 mmol of CH_4; 160 °C for 120 h led to another 0.269 mmol of CH_4. In all, 0.994 mmol of CH_4 was formed. The material remaining in the tube after pyrolysis consisted of a gray solid, a viscous liquid, which was soluble in dimethoxyethane, and a "silver"-colored mirror of gallium metal. These results suggest extensive decomposition and partial reduction of the sample to gallium metal. It is interesting that KH and NaH give slightly different results. However, there is no evidence for the formation of a characterizable product by a simple, well-defined reductive-elimination reaction.

The observed chemistry of $In(CH_3)_3$ with NaH and KH leads to the same conclusions as those proposed for $Al(CH_3)_3$ and $Ga(CH_3)_3$. When 1 mmol of $In(CH_3)_3$ was combined with excess KH in benzene at 25 °C, 0.159 mmol of CH_4 and a gray-black solid were formed after 12 h. The reaction of $In(CH_3)_3$ with NaH in dimethoxyethane at 130 °C for 12 h produced 0.120 mmol of CH_4 and a black insoluble solid. It is of interest to compare our results with those of Gavrilenko, Kolesov, and Zakharin.[15] They reported that $In(CH_3)_3$ reacted with NaH and KH to form $NaIn(CH_3)_3H$ and $KIn(CH_3)_3H$. Heating to 100 °C led to the formation of $NaIn(CH_3)_4$. It is difficult to reconcile our results but all data suggest that a simple, stoichiometric, reductive-elimination reaction is not the only reaction occurring.

All of the results from the investigations of the reactions of group 3 organometallic compounds with alkali-metal hydrides suggest that reductive-elimination reactions can occur. The facility of the reaction depends on the alkali-metal hydride, the organic substituent, and the group 3 element. However, low oxidation state compounds are not the only product. The high temperatures required to initiate the reductive-elimination reaction for the aluminum compounds and the methyl derivatives lead to apparent decomposition reactions, which occur prior to or after the reduction reaction.

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Registry No. $Al(CH_2SiMe_3)_3$, 41924-27-0; $KAl(CH_2SiMe_3)_3H$, 80594-56-5; $KGa(CH_3)_3H$, 41575-37-5; $KAl(CH_3)_3H$, 53108-65-9; $KIn(CH_3)_3H$, 63213-62-7; $Ga(CH_3)_3$, 1445-79-0; $Al(CH_3)_3$, 75-24-1; $In(CH_3)_3$, 3385-78-2; KH, 7693-26-7; NaH, 7646-69-7; $LiCH_2SiMe_3$, 1822-00-0; $AlBr_3$, 7727-15-3.

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Aqueous Nitrosyliron(II) Chemistry. 1. Reduction of Nitrite and Nitric Oxide by Iron(II) and (Trioxodinitrato)iron(II) in Acetate Buffer. Intermediacy of Nitrosyl Hydride[1]

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Nitrite is reduced by Fe(II) sequentially to NO and N_2O at pH 5 (acetate buffer), and N_2 is not a product under these conditions. The nitrosyl complex $FeNO^{2+}$ is stable against reduction to N_2O below pH ca. 4; the threshold for reduction to N_2 occurs at ca. pH 8. The decomposition of $HN_2O_3^-$ is retarded by coordination to Fe(II) at pH 5 and 6 but produces the same products as "free" trioxodinitrate, N_2O and NO_2^-. The latter species is reduced by Fe(II), and nitrogen mass balance shows that some $HN_2O_3^-$ remains undecomposed, probably in coordination to Fe(III). A ^{15}N tracer experiment at pH 6 shows that N_2O product arises initially from Fe(II)-coordinated $HN_2O_3^-$ with both N atoms contributing to a random distribution, i.e. scrambled but still derived from an HNO precursor as in the case of uncoordinated $HN_2O_3^-$. Reduction of $^{15}N^{18}O$ by Fe(II) at pH 6 in the presence of $HN_2O_3^-$ (natural abundance) gives rise to N_2O, whose isotopic composition shows both self-dimerization and comingling dimerization of HNO from two sources, demonstrating that HNO is a primary product of the Fe(II) reduction of NO.

The reduction of nitrous acid by Fe(II) has been the subject of a number of previous investigations;[2-7] its products are known to include NO at low pH, with N_2O, N_2, and NH_3 appearing at successively higher pH levels whose thresholds have not been sharply established. Brown and Drury[6] have reported quantitative reduction of NO_2^- to NH_3 by excess $Fe(OH)_2$ in NaOH solution and proposed a sequential process involving the intermediate formation of HNO and NH_2OH at oxidation states +1 and −1, respectively. Chalamet[7] has reported NO, N_2O, and N_2 to be the reaction products at pH 5 in acetate buffer and proposed that NO and N_2O result from sequential single-electron-transfer reactions but that N_2 production is a separate, direct process.

If NO is produced in the presence of Fe(II), the well-known "brown ring" complex $Fe(H_2O)_5NO^{2+}$ forms, and reduction of NO by Fe(II) may therefore be influenced by the properties of this species. The composition of this complex has been known since early in this century.[8,9] Its UV spectrum is known to be independent of the anion present.[10] Oxidation of $FeNO^{2+}$ to Fe(III) by NO was reported in 1924[11] and NO

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