stretching, deformation, and rocking frequencies observed for hydridonickel methyl are also included in Table IV and further substantiate the presence of a methyl group. This was also indirect evidence of an $NiCH_3$ group, as no frequency was observed in the Ni–C stretching region. The CH_2 wagging frequency, 937.7 cm^{-1}, was identical with that observed for the vinyl group in vinylnickel hydroxide, C_2H_3NiOH, and corroborated the presence of a vinyl group. We have thus assigned the structure of vinylnickel methyl, $C_2H_3NiCH_3$, to this UV product.

Upon extended UV photolysis, the peaks assigned to $C_2H_3NiCH_3$ decreased and methane was produced. The other decomposition product(s), having a total empirical formula of C_2H_2Ni, is (are) unknown. Possible candidates would be $NiCCH_2$ and $Ni(C_2H_2)$. Nickel and acetylene have been shown to form an $Ni(C_2H_2)$ π complex which rearranged to $NiCCH_2$, nickel vinylidene, with $\lambda \geq 400$ nm irradiation.[35] $NiCCH_2$ was unstable in UV irradiation and photoreverted to the nickel acetylene π complex. However, the absence of frequencies assignable to either an $Ni(C_2H_2)$ π complex or $NiCCH_2$ with the disappearance of $C_2H_3NiCH_3$ suggests a different photofragmentation product. One possibility is the production of nickel carbide and hydrogen. The infrared spectrum of nickel carbide has not been measured and could be quite difficult to detect.

The stability of $CD_2Ni(C_2D_4)$ toward $\lambda \geq 400$ nm and UV irradiation indicates a strong kinetic isotope effect, as expected for a hydrogen shift. The photofragmentation of $CH_2Ni(C_2H_4)$ and production of methane both involve a hydrogen shift.

Conclusions

1. The isolation and characterization of the first unligated nickelacyclobutane have been accomplished by using matrix-isolation FTIR spectroscopy. C–C bond activation of cyclopropane, oxidative addition to a nickel atom, and metallacyclobutane formation have been demonstrated.

2. Nickelacyclobutane underwent metathesis to methylenenickel (ethylene) π complex with $\lambda \geq 500$ nm irradiation. The presence of a metal atom has been shown to lower the energy for the decomposition of cyclopropane to methylene and ethylene, a highly endothermic process requiring 92.0 kcal/mol.

3. With UV photolysis $CH_2Ni(C_2H_4)$ underwent C–H bond activation of ethylene and rearranged to vinylnickel methyl. $C_2H_3NiCH_3$ ultimately decomposed, releasing methane. The stepwise decomposition of an industrially significant molecule, cyclopropane, to methane has been accomplished at a single metal atom center at cryogenic temperatures.

Acknowledgment. The authors would like to thank the National Science Foundation and Robert A. Welch Foundation for financial support.

Registry No. C_3H_6, 75-19-4; C_3D_6, 2207-64-9; Ni, 7440-02-0; $CD_2Ni(C_2D_4)$, 114199-03-0; $CH_2Ni(C_2H_4)$, 114199-04-1; $C_2H_3NiCH_3$, 114199-05-2; nickelacyclobutane, 114199-01-8; nickelacyclobutane-d_6, 114199-02-9; methane, 74-82-8.

---

[35] Kline, E. S.; Kafafi, Z. H.; Hauge, R. H.; Margrave, J. L. *J. Am. Chem. Soc.* 1987, *109*, 2402.

Synthesis and Characterization of Neopentylgallium Compounds

O. T. Beachley, Jr.,* and J. C. Pazik

Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214

Received October 21, 1987

The series of neopentylgallium compounds, $Ga(CH_2CMe_3)_3$, $Ga(CH_2CMe_3)_2Cl$, $Ga(CH_2CMe_3)_2Br$, $Ga(CH_2CMe_3)Cl_2$, and $Ga(CH_2CMe_3)I_2$ have been prepared by very facile, high-yield routes, have been easily purified, and have been fully characterized. The new compound $Ga(CH_2CMe_3)_3$ is a nonpyrophoric liquid that exists as monomeric, three-coordinate gallium species in benzene solution. Cryoscopic molecular weight studies indicate that $Ga(CH_2CMe_3)_2Cl$, $Ga(CH_2CMe_3)Cl_2$, and $Ga(CH_2CMe_3)Br_2$ are dimeric in benzene solution. Consequently, it is noteworthy that an equimolar mixture of $[Ga(CH_2CMe_3)_2Cl]_2$ and $[Ga(CH_2CMe_3)Cl_2]_2$ does not undergo a rapid exchange reaction at room temperature as four ^1H NMR lines are observed. A comparison of the properties of the neopentyl- and [(trimethylsilyl)methyl]gallium derivatives suggest that the neopentyl group has larger steric effects and stronger electron-withdrawing properties than the corresponding (trimethylsilyl)methyl substituents.

Introduction

The utilization of compound semiconductors for electronic and optical devices can be related to the development of epitaxial growth techniques.[1] The technique of choice for preparing compound semiconductors such as GaAs, GaP, and GaSb is organometallic vapor-phase epitaxy or organometallic chemical vapor deposition. Since only a surprisingly few organogallium compounds, $GaMe_3$ and $GaEt_3$, are readily available as gallium sources, our research program has been directed toward the synthesis and characterization of new organogallium compounds. In order for a gallium compound to be a useful gallium source, the compound should be readily prepared and easily purified as well as be a volatile liquid with excellent thermal stability at room temperature. In this paper, we report the synthesis and characterization of a series of organogallium compounds that incorporate the neopentyl (CH_2CMe_3 = Np) group including $GaNp_3$, $GaNp_2Cl$, $GaNp_2Br$, $GaNpCl_2$, and $GaNpI_2$. These neopentylgallium derivatives are of chemical interest because the bulky neopentyl substituent with no β-hydrogen atoms might introduce unusual chemical properties. Furthermore, direct comparisons between corresponding neopentyl and

---

[1] Kuech, T. F. *Mat. Sci. Rep.* 1987, *2*, 3.

0276-7333/88/2307-1516$01.50/0

(trimethylsilyl)methyl[2] derivatives might enhance our understanding of the electronic and steric effects of these organic substituents in organogallium chemistry.

Experimental Section

All compounds described in this investigation were extremely sensitive to oxygen and moisture and were manipulated in a standard vacuum line or in a purified argon atmosphere. All solvents were purified before use. Gallium(III) chloride was purified by sublimation under high vacuum at 70–80 °C immediately prior to use. The compound GaI_3 was prepared from gallium metal and iodine in refluxing toluene, a modification of the method of Tuck and Freeland.[3] Neopentyl chloride was purchased from Fairfield Chemical Co. and was distilled prior to use. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY. Infrared spectra of Nujol mulls between CsI plates were recorded by means of a Perkin-Elmer 683 spectrometer. Absorption intensities are reported with the abbreviations vs (very strong), s (strong), m (medium), w (weak), and sh (shoulder). The ^1H NMR spectra were recorded at 90 MHz by using a Varian Model EM-390 spectrometer. All samples for NMR spectra were contained in sealed NMR tubes. Chemical shifts are reported in δ units (ppm) and are referenced to $SiMe_4$ as δ 0.00 and benzene as δ 7.13. Melting points were observed in sealed capillaries. Molecular weights were measured cryoscopically in benzene by using an instrument similar to that described by Shriver.[4]

Synthesis of $GaNp_3$. In a typical synthetic experiment, the Grignard reagent, NpMgCl, was prepared from magnesium turnings (5.802 g, 238.6 mmol) and freshly distilled neopentyl chloride (24.22 g, 227.2 mmol) in 100 mL of diethyl ether. Even though the magnesium had been activated with iodine without stirring prior to the addition of the neopentyl chloride/ether solution, the reaction mixture was refluxed for 18 h. Then a flask charged with 9.58 g of freshly sublimed $GaCl_3$ (54.4 mmol) dissolved in 250 mL of dry diethyl ether was fitted with a condenser, mechanical stirrer, and a pressure equalizing addition funnel. Under a cover of argon the Grignard solution was transferred to the addition funnel and was added to the $GaCl_3$ solution over a period of 20 min. After the addition was complete, the reaction mixture was stirred at room temperature for 18 h. The stirrer, condenser, and addition funnel were replaced by stoppers and a Teflon valve/adapter. The Et_2O was then removed by vacuum distillation at room temperature. The crude product, a $GaNp_3/Et_2O$ mixture, was isolated by vacuum distillation at 125 °C into a side-arm flask (cooled to −196 °C) attached to the reaction flask by means of an 85° bent elbow. The distillation was continued for approximately 5 h. The Et_2O was then removed from the crude product by a simple vacuum distillation at room temperature for 1 h. The product was finally purified by vacuum distillation in a short-path still at 55 °C (0.001 mm, dynamic vacuum). Pure $GaNp_3$ was obtained as a colorless, nonpyrophoric liquid (14.0 g, 49.6 mmol, 91.1% yield based on $GaCl_3$). $Ga(CH_2CMe_3)_3$: ^1H NMR (C_6H_6, δ) 1.06 (s, 27 H, $-CMe_3$), 1.01 (s, 6 H, $-CH_2-$); IR (neat liquid, cm^{-1}) 2950 (vs), 2900 (vs), 2860 (vs), 2650 (w), 1468 (s), 1461 (s), 1398 (m), 1382 (m), 1358 (vs), 1229 (s), 1132 (m), 1095 (m), 1031 (m), 1006 (s), 928 (w), 909 (w), 735 (m), 703 (m), 610 (m), 591 (m), 570 (m), 460 (sh), 450 (m), 380 (m), 310 (m), 287 (m). Anal. Calcd: C, 63.63; H, 11.75. Found: C, 63.64; H, 11.68. Cryoscopic molecular weight, benzene solution, formula weight 283 (obsd molality, obsd mol wt, association): 0.0770, 275, 0.965; 0.0610, 291, 1.03; 0.0510, 304, 1.07. Solubility: soluble in ether, THF, benzene, and pentane. Trineopentylgallium(III) does not form stable 1:1 adducts with either THF or Et_2O.

Synthesis of $GaNp_2Cl$. Trineopentylgallium(III) (2.93 g, 10.4 mmol) was weighed in the drybox into a tared, screw-cap vial, and 0.911 g of freshly sublimed $GaCl_3$ (5.18 mmol) was placed in a second tared vial. Both compounds were dissolved in pentane and then were pipetted into a 100-mL side-arm flask. Each vial was rinsed several times (5–7) with fresh aliquots of pentane to ensure the quantitative transfer of the reagents. The flask was then stoppered, cooled to −196 °C, and then evacuated. After being stirred at room temperature for 18 h, the slightly cloudy solution was filtered through a fine glass frit. The pentane was removed by vacuum distillation, and $GaNp_2Cl$ was obtained as a colorless solid in nearly quantitative yield (3.65 g, 14.7 mmol, 95.0% yield). The compound was further purified by recrystallization from pentane at −78 °C. $GaNp_2Cl$: mp 70.0–71.5 °C; ^1H NMR (C_6H_6, δ) 1.10 (s, 18 H, $-CMe_3$), 1.31 (s, 4 H, $-CH_2-$); IR (Nujol mull, cm^{-1}) 2718 (vw), 2380 (vw), 2284 (vw), 1983 (vw), 1736 (vw), 1258 (sh), 1234 (vs), 1142 (m), 1100 (m), 1018 (m), 1002 (m), 932 (w), 914 (vw), 802 (vw), 742 (m), 725 (vs), 704 (m), 639 (s), 593 (w), 459 (w), 450 (w), 385 (w), 360 (sh), 298 (m). Anal. Calcd: C, 48.54; H, 8.96. Found: C, 48.44; H, 9.26. Cryoscopic molecular weight, benzene solution, formula weight 247.5 (obsd molality, obsd mol wt, association): 0.0799, 520, 2.10; 0.0608, 510, 2.06; 0.0458, 503, 2.03. Solubility: soluble in pentane, benzene Et_2O, and THF. The compound $GaNp_2Cl$ does not form stable 1:1 adducts with either THF or Et_2O.

Synthesis of $GaNp_2Br$. Reaction of 0.296 g of $GaBr_3$ (0.956 mmol) with 0.544 g of $GaNp_3$ (1.92 mmol) in pentane solution yielded 0.657 g of the colorless, crystalline solid $GaNp_2Br$ (2.25 mmol, 78.5% based on the initial amount of gallium). To facilitate the dissolution of $GaBr_3$ in pentane, a small amount of the pentane solution of $GaNp_3$ was added to the vial containing the $GaBr_3$. This vial was then rinsed several times to ensure the quantitative transfer of the reagents. Purification was as described for $GaNp_2Cl$.

$GaNp_2Br$: mp 68.5–70.0 °C; ^1H NMR (C_6H_6, δ) 1.11 (s, 18 H, $-CMe_3$), 1.47 (s, 4 H, $-CH_2-$); IR (Nujol mull, cm^{-1}) 1360 (vs), 1258 (vw), 1233 (s), 1140 (w), 1098 (w), 1015 (w), 1000 (m), 930 (vw), 910 (vw), 800 (vw), 740 (m), 722 (s), 696 (m), 635 (m), 590 (vw), 455 (w), 383 (w), 360 (vw), 295 (w). Anal. Calcd: C, 41.15; H, 7.60. Found: C, 40.85; H, 7.45. Cryoscopic molecular weight, benzene solution, formula weight 291.9 (obsd molality, obsd mol wt, association): 0.0729, 646, 2.21; 0.0593, 650, 2.23; 0.0503, 645, 2.21. Solubility: soluble in pentane, benzene, THF, and Et_2O.

Synthesis of $GaNpCl_2$. In a typical reaction 1.11 g of freshly sublimed $GaCl_3$ (6.33 mmol) was reacted in pentane with 0.897 g of $GaNp_3$ (3.17 mmol) to produce 1.72 g of pure $GaNpCl_2$ (8.12 mmol, 85.5% yield based on the initial amount of gallium). The compound can be further purified as described for $GaNp_2Cl$ or by vacuum distillation (0.001 mm) in a short-path still at 71 °C. $GaNpCl_2$: mp 29.0–31.0 °C; ^1H NMR (C_6H_6, δ) 0.91 (s, 8 H, $-CMe_3$), 1.25 (s, 2 H, $-CH_2-$); IR (Nujol mull, cm^{-1}): 3410 (vw), 3355 (vw), 2720 (w), 2675 (vw), 2400 (vw), 2290 (vw), 2110 (vw), 2005 (vw), 1970 (vw), 1868 (vw), 1780 (vw), 1730 (vw), 1550 (vw), 1362 (vw), 1263 (m), 1233 (vs), 1140 (s), 1098 (m), 1015 (m), 1002 (s), 928 (vw), 910 (vw), 845 (m), 808 (m), 729 (vs), 631 (s), 562 (vw), 528 (vw), 455 (m), 397 (vs), 372 (vs), 252 (vs). Anal. Calcd: C, 28.36; H, 5.24. Found: C, 28.36; H, 5.15. Cryoscopic molecular weight, benzene solution, formula weight 211.8 (obsd molality, obsd mol wt, association): 0.0816, 423, 2.00; 0.0591, 422, 1.99; 0.0445, 418, 1.97. Solubility: soluble in pentane, benzene, THF, and Et_2O. The compound $GaNpCl_2$ formed a stable 1:1 adduct with THF.

Lewis Acidity Studies. The abilities of $GaNp_3$, $GaNp_2Cl$, and $GaNpCl_2$ to form Lewis acid–base adducts with NMe_3 have been investigated. In a typical experiment an excess of Lewis base was vacuum distilled onto a weighed quantity of the Lewis acid. After the resulting sample was warmed to room temperature, the excess base was removed. A mass measurement on the resulting product was used to determine the quantity of base which reacted. The mole ratio of the Lewis acid–base which reacted, the melting point of the resulting adduct, and the ^1H NMR spectrum were used to support the formation of adducts. (Since THF was used as a solvent, the formation of adducts is included in sections on the individual compounds.) The following observations for NMe_3 were made.

Np_3GaNMe_3: $GaNp_3/NMe_3$ mole ratio was inconclusive because the adduct appeared slightly volatile at room temperature (possibly related to dissociation); mp 100–108 °C; ^1H NMR (C_6H_6, δ) 0.74 (s, 6.0 H, CH_2), 1.25 (s, 28.0 H, CMe_3), 1.73 (s, 9.0 H, NMe_3).

$ClNp_2GaNMe_3$: $GaNp_2Cl/NMe_3$ mole ratio (mass measurements) 1.06; mp 85.7–88.2 °C; ^1H NMR (C_6H_6, δ) 0.71 (s, 4.1 H,

---

[2] Beachley, O. T., Jr.; Simmons, R. G. *Inorg. Chem.* **1980**, *19*, 1021.

[3] Freeland, B. H.; Tuck, D. G. *Inorg. Chem.* **1976**, *15*, 475.

[4] Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air-Sensitive Compounds*; Wiley: New York, 1986; p 38.

CH_2), 1.34 (s, 17.2 H, CMe_3), 1.82 (s, 9.0 H, NMe_3). Resonance for methylene protons is a doublet (J = 6 Hz with a 300-MHz Bruker spectrometer).

$Cl_2NpGaNMe_3$: $GaNpCl_2/NMe_3$ mole ratio (mass measurements) 1.02; mp 61.0–70.0 °C; ^1H NMR (C_6H_6, δ) 0.83 (s, 1.80 H, CH_2), 1.23 (s, 8.23 H, CMe_3), 1.82 (s, 9.0 H, NMe_3).

Synthesis of $GaNpI_2$. Because of the low solubility of GaI_3 in pentane, benzene was used as the reaction solvent. A 0.882-g sample of GaI_3 (1.956 mmol) was transferred as a solid to a 100-mL side-arm flask, and the remaining traces of GaI_3 were rinsed into the flask with an aliquot of benzene. The sample of $GaNp_3$ (0.277 g, 0.978 mmol) was dissolved in benzene and transferred into the reaction flask as described in the synthetic procedure for $GaNp_2Cl$. After the solution was at ambient temperature for 18 h, the benzene was removed by vacuum distillation to yield a slightly pink, viscous liquid. The final traces of benzene were removed from the product by dissolving the sample in 25 mL of pentane and then by removing all volatile components under high vacuum. This process was repeated. The final product $GaNpI_2$ (0.886 g, 2.25 mmol) was isolated as a slightly pink solid in 76.5% yield based on the initial amount of gallium present. An analytically pure sample as a pale pink solid was obtained by recrystallization from pentane at −78 °C. $GaNpI_2$: mp 72.0–75.0 °C; ^1H NMR (C_6H_6, δ): 0.99 (s, 9 H, $-CMe_3$), 1.90 (s, 2 H, $-CH_2-$); IR (Nujol mull, cm^{-1}) 1363 (s), 1262 (vw), 1235 (vs), 1132 (m), 1092 (m), 1026 (m), 999 (m), 928 (vw), 910 (vw), 833 (vw), 809 (vw), 743 (w), 721 (vs), 614 (m), 452 (w), 383 (w), 288 (m). Anal. Calcd: C, 15.22; H, 2.81. Found: C, 15.40; H, 2.97. Solubility: soluble in benzene, pentane, and THF. The compound $GaNpI_2$ forms a stable 1:1 adduct with THF.

Synthesis of $Ga(CH_2SiMe_3)_2Cl$. The synthesis of $Ga(CH_2SiMe_3)_2Cl$ was as described for the preparation of $GaNp_2Cl$. The reaction of 0.994 g of $Ga(CH_2SiMe_3)_3$ (3.00 mmol) with 0.265 g of freshly sublimed $GaCl_3$ (1.51 mmol) produced $Ga(CH_2SiMe_3)_2Cl$ in nearly quantitative yield (1.17 g, 4.19 mmol, 92.5% yield based on the amount of gallium used). Purification was achieved by recrystallization from pentane at −78 °C. $Ga(CH_2SiMe_3)_2Cl$: mp 27–29 °C; ^1H NMR (C_6H_6, δ) 0.15 (s, 18 H, $-SiMe_3$), 0.20 (s, 4 H, $-CH_2-$); IR (Nujol mull, cm^{-1}) 2952 (vs), 2895 (m), 1935 (vw), 1868 (vw), 1445 (w), 1420 (sh), 1414 (sh), 1403 (w), 1353 (w), 1302 (w), 1259 (s), 1245 (vs), 1001 (s), 958 (sh), 850 (vs), 825 (vs), 758 (s), 720 (s), 683 (m), 622 (m), 610 (w), 593 (m), 579 (m), 560 (m), 512 (w), 228 (s). Anal. Calcd: C, 34.36; H, 7.93. Found: C, 33.99; H, 7.56. Cryoscopic molecular weight, benzene solution, formula weight 279.6 (obsd molality, obsd mol wt, association): 0.0730, 574, 2.05; 0.0542, 570, 2.04; 0.0361, 571, 2.04. Solubility: soluble in pentane, benzene, and THF.

Synthesis of $Ga(CH_2SiMe_3)Cl_2$. The procedure for the synthesis of $Ga(CH_2SiMe_3)Cl_2$ was similar to that used to prepare $GaNp_2Cl$. Addition of 0.914 g of $Ga(CH_2SiMe_3)_3$ (2.76 mmol) to 0.973 g of freshly sublimed $GaCl_3$ (5.53 mmol) in pentane solution produced 1.46 g of $Ga(CH_2SiMe_3)Cl_2$ (6.39 mmol, 77.2% yield based on the amount of gallium used). The colorless solid $Ga(CH_2SiMe_3)Cl_2$ was purified by recrystallization from pentane at −40 °C. $Ga(CH_2SiMe_3)Cl_2$: mp 55.0–56.8 °C (lit.[2] 48.0–49.0 °C); ^1H NMR (C_6H_6, δ) 0.01 (s, 9, $SiMe_3$), 0.14 (s, 2 H, $-CH_2-$); IR (Nujol mull, cm^{-1}) 3790 (vw), 3725 (vw), 3660 (vw), 3498 (vw), 2725 (w), 2680 (w), 2485 (vw), 2360 (vw), 2100 (vw), 2035 (vw), 2000 (vw), 1945 (w), 1875 (w), 1810 (vw), 1740 (vw), 1648 (vw), 1578 (vw), 1405 (s), 1345 (vs), 1323 (m), 1247 (vs), 1020 (vs), 1009 (vs), 973 (m), 837 (vs, br), 787 (s), 755 (vs, br), 720 (vs), 688 (vs), 662 (w), 621 (s), 598 (vs), 558 (vs), 480 (vw), 463 (w), 380 (vs), 350 (vs), 298 (vs). Anal. Calcd: C, 21.09; H, 4.87. Found: C, 21.27; H, 5.01. Solubility: soluble in benzene and pentane.

Results and Discussion

A series of neopentylgallium compounds including $GaNp_3$, $GaNp_2Cl$, $GaNp_2Br$, $GaNpCl_2$, and $GaNpI_2$ have been prepared by very facile, high-yield routes, have been easily purified, and have been fully characterized. The properties of these neopentyl compounds have also been compared with the corresponding (trimethylsilyl)methyl derivatives. In cases in which the previously reported properties of [(trimethylsilyl)methyl]gallium derivatives[2] were inconsistent with those of the corresponding neopentyl derivative, the synthesis and characterization of the [(trimethylsilyl)methyl]gallium derivative was reinvestigated. The characterization data for the neopentyl derivatives and the reinvestigated (trimethylsilyl)methyl derivatives included physical properties, elemental analyses, cryoscopic molecular weight measurements, Lewis acid–base studies, and infrared and NMR spectra.

Trineopentylgallium(III) has been prepared from $GaCl_3$ by a typical Grignard reaction in diethyl ether solution and has been readily isolated by vacuum distillation at 55 °C. For the synthetic reaction to be successful a 25% calculated excess of the Grignard reagent over $GaCl_3$, assuming complete reaction, was required. Our experimental data suggested that the reaction between the neopentyl chloride and magnesium proceeded to only 75% completion. It is of interest that $GaNp_3$ is a nonpyrophoric, colorless liquid. In comparison, $Ga(CH_2SiMe_3)_3$[2] and most other gallium alkyls[5] are pyrophoric liquids. Molecular weight studies suggest that $GaNp_3$ exists as monomeric species in benzene solution. In Lewis acidity studies, neither of the oxygen bases Et_2O nor THF formed stable 1:1 adducts with $GaNp_3$, whereas THF formed an adduct with $Ga(CH_2SiMe_3)_3$. It is also noteworthy that the stronger base NMe_3 forms an apparent adduct with $Ga(CH_2SiMe_3)_3$ and probably with $GaNp_3$. These observations suggest that the neopentyl group has significantly greater steric effects than does the (trimethylsilyl)methyl group. Alternatively, electronic effects may be responsible for the increased Lewis acidity of $Ga(CH_2SiMe_3)_3$. However, the results of our studies in organoaluminum chemistry[6] suggest that the neopentyl group has stronger electron-withdrawing properties and larger steric effects than the (trimethylsilyl)methyl group.

The neopentylgallium(III) halides $GaNp_2X$ (X = Cl, Br) and $GaNpY_2$ (Y = Cl, I) have been prepared by stoichiometric ligand redistribution reactions between $GaNp_3$ and the appropriate gallium(III) halide. The ligand redistribution reaction has proven to be a convenient method for preparing the neopentylgallium(III) halide compounds provided that stoichiometric quantities of reagents are employed. Excess quantities of either $GaNp_3$ or the gallium(III) halide will result in the formation of additional inseparable products. Pentane is the solvent of choice for the ligand redistribution reactions involving GaX_3 (X = Cl, Br). These gallium halides are soluble in pentane, and pentane is easily removed from the nonvolatile reaction products. In contrast, GaI_3 is insoluble in pentane. Therefore, $GaNpI_2$ was prepared from $GaNp_3$ and GaI_3 in a 1:2 mol stoichiometry in benzene solution.

The neopentylgallium(III) halides have been fully characterized. The compounds $GaNpCl_2$, $GaNp_2Cl$, and $GaNp_2Br$ are colorless solids whereas $GaNpI_2$ is a light pink solid at room temperature. Neopentylgallium(III) dichloride has a low melting point (29.0–31.0 °C). Since the melting point is only slightly above room temperature, the compound has been observed to exist as either a crystalline solid, a liquid, or more commonly a sticky solid. In order to minimize the problems associated with handling a sticky solid, samples of $GaNpCl_2$ were heated to form a mobile liquid prior to entry into the drybox. It is of experimental importance that heated samples remained liquid for a reasonable length of time, about 1 h or more, before crystallization. Cryoscopic molecular weight measurements indicate that the neopentylgallium(III) halide compounds ($GaNp_2Cl$, $GaNp_2Br$, and $GaNpCl_2$) are di-

---

(5) Coates, G. E.; Green, M. L. H.; Wade, K. *Organometallic Compounds*; 3rd ed.; Metheun: London, 1967; Vol. 1, p 343.

(6) Beachley, O. T., Jr.; Victoriano, L. *Organometallics* 1988, 7, 63.

meric in benzene solution. The most likely structure for a dimeric molecule of this type would involve halogen donor–acceptor bridge bonds. The apparent existence of halogen bridge bonds in solution suggests that the gallium atom is not sufficiently hindered by the bulky neopentyl groups to preclude dimer formation. The dimeric nature of $GaNp_2Cl$ in solution indicates it is not as weak as Lewis acid as $Ga(C_5Me_5)_2Cl$, a molecule which is dimeric in the solid state but apparently monomeric in solution.[7] Our studies indicate that $GaNp_2Cl$ is a relatively weak Lewis acid. The compound forms a stable 1:1 adduct with NMe_3 but not with THF, a slightly weaker Lewis base. The only other gallium compounds that do not form stable adducts with THF are $GaMes_3$ (Mes = mesityl),[8] $Ga(C_5Me_5)_2Cl$,[7] and $Ga(C_5Me_5)_3$.[9] The dihalide derivative $GaNpCl_2$ is a stronger Lewis acid than $GaNp_2Cl$ and forms stable 1:1 adducts with both NMe_3 and THF. The iodide derivative $GaNpI_2$ also forms a 1:1 adduct with THF.

The halide derivatives $GaNp_2X$ (X = Cl, Br) and $GaNpY_2$ (Y = Cl, I) exhibit characteristic ^1H NMR spectra in benzene solution with the resonances for the methylene protons being downfield of that for the methyl protons for a given compound. Similar observations of the relative chemical shifts of methylene and methyl protons have been reported for benzene solutions of the (trimethylsilyl)methyl halogen derivatives of gallium and indium[10] but not for the (trimethylsilyl)methyl[11] or neopentyl[6] derivatives of aluminum. Other gallium halogen compounds which have methylene and methyl protons in a given substituent also exhibit other patterns. For example, the ^1H NMR spectrum of $Ga(i\text{-}Bu)_2Cl$ (neat with sufficient benzene or CH_2Cl_2 for reference)[12] exhibited only one resonance; the lines for the both types of protons were coincident, whereas the line for the methylene protons of $GaEt_2Cl$ (CCl_4 with TMS as reference)[13] was upfield of that for the methyl line. The significance of these observations is uncertain and will be investigated further as more examples of these types of compounds are characterized.

The ^1H NMR spectrum of a mixture of $GaNp_2Cl$ and $GaNpCl_2$ in benzene exhibited four resonances at 1.33, 1.23, 0.99, and 0.95 ppm for the four different types of protons in the two molecules. The lines at 1.33 and 0.99 ppm are assigned to the methylene and methyl groups of $GaNp_2Cl$, respectively, whereas the lines at 1.23 and 0.95 ppm are assigned to the methylene and methyl groups, respectively, of $GaNpCl_2$. Although the resonances for the protons of the methyl groups are shifted upfield relative to their positions in the spectra of the pure compounds, the chemical shifts of the methylene protons are in excellent agreement with those observed in the spectra of pure $GaNp_2Cl$ and $GaNpCl_2$.

The observation that bisneopentylgallium(III) chloride existed as simple dimer in solution prompted a reinvestigation of the synthesis and properties of the [(trimethylsilyl)methyl]gallium(III) chlorides, $Ga(CH_2SiMe_3)_nCl_{3-n}$ (n = 1, 2). The monochloro derivative $Ga(CH_2SiMe_3)_2Cl$ was of particular interest because it had been reported to be a high melting, insoluble solid with a possibly polymeric structure.[2] In our current studies, $Ga(CH_2SiMe_3)_2Cl$ has been prepared in 92.5% yield as a colorless, crystalline solid from the reaction of $Ga(CH_2SiMe_3)_3$ and $GaCl_3$ in a 2:1 mol ratio. An analytically pure sample of $Ga(CH_2SiMe_3)_2Cl$ had a low melting point, 27–29 °C. Like $GaNpCl_2$, $Ga(CH_2SiMe_3)_2Cl$ is best handled as a liquid. In fact, all the properties of $Ga(CH_2SiMe_3)_2Cl$ are quite similar to those of $GaNp_2Cl$. Bis[(trimethylsilyl)methyl]gallium chloride is very soluble in pentane, benzene, and THF. Cryoscopic molecular weight measurements indicate that $Ga(CH_2SiMe_3)_2Cl$ is dimeric in benzene solution over a concentration range of 0.0730–0.0361 m. The ^1H NMR spectrum exhibits two resonances at 0.15 and 0.20 ppm for the methyl and methylene protons, respectively. The material previously reported to be $Ga(CH_2SiMe_3)_2Cl$ was prepared in approximately 50% yield by a elimination reaction between $Ga(CH_2SiMe_3)_3$ and anhydrous HCl.[2] The product was reported to exhibit a high melting point (159.5–160.0 °C) and to be insoluble in pentane and benzene.[2] In addition to the discrepencies between the melting points and solubility data, the IR spectroscopic data for the two independently prepared samples are also in disagreement. Therefore, it is likely that the previous synthesis[2] did not yield $Ga(CH_2SiMe_3)_2Cl$ but perhaps some air-oxidized or hydrolyzed product.

The synthesis and characterization of [(trimethylsilyl)methyl]gallium(III) dichloride, $Ga(CH_2SiMe_3)Cl_2$, has also been reinvestigated. The compound was previously isolated from a ligand redistribution reaction between $Ga(CH_2SiMe_3)_3$ and $GaCl_3$ in a 1:2 mol ratio in benzene solution.[2] In the current study, $Ga(CH_2SiMe_3)Cl_2$ has also been independently synthesized by the stoichiometric ligand redistribution reaction as a colorless solid in 77.2% yield. It is noteworthy that the melting point of the crude product (48.5–51.5°C) corresponds to the value previously reported[2] for the purified compound (48–49 °C). Upon recrystallization of the crude product from a pentane solution at −40 °C, an analytically pure sample of $Ga(CH_2SiMe_3)Cl_2$ had a melting point of 55.0–56.8 °C. The IR spectrum of an analytically pure sample of $Ga(CH_2SiMe_3)Cl_2$ did not coincide with that previously reported.[2] The earlier spectroscopic data would be in doubt if it were based on an impure sample of $Ga(CH_2SiMe_3)Cl_2$.

Acknowledgment. This work was supported in part by the Office of Naval Research. We thank Matthew J. Noble, University at Buffalo, and Henry J. Gysling, Eastman Kodak Co., for assistance with Lewis acidity studies which used NMe_3.

Registry No. $GaNp_3$, 106136-97-4; $GaNp_2Cl$, 113976-09-3; $GaNp_2Br$, 113976-10-6; $GaNpCl_2$, 113976-11-7; Np_3GaNMe_3, 113976-13-9; $ClNp_2GaNMe_3$, 113976-14-0; $Cl_2NpGaNMe_3$, 113976-15-1; $GaNpI_2$, 113976-12-8; $Ga(CH_2SiMe_3)_2Cl$, 72708-38-4; $Ga(CH_2SiMe_3)Cl_2$, 74251-16-4; NpCl, 753-89-9; NpMgCl, 13132-23-5; $GaCl_3$, 13450-90-3; $GaBr_3$, 13450-88-9; $GaNpCl_2{\cdot}THF$, 113976-16-2; GaI_3, 13450-91-4; $Ga(CH_2SiMe_3)_3$, 72708-53-3; $GaNpI_2{\cdot}THF$, 113976-17-3.

---

(7) Beachley, O. T., Jr.; Hallock, R. B.; Zhang, H. M.; Atwood, J. L. *Organometallics* **1985**, *4*, 1675.

(8) Beachley, O. T., Jr.; Churchill, M. R.; Pazik, J. C.; Ziller, J. W. *Organometallics* **1986**, *5*, 1814.

(9) Beachley, O. T., Jr.; Hallock, R. B. *Organometallics* **1987**, *6*, 170.

(10) Beachley, O. T., Jr.; Rusinko, R. N. *Inorg. Chem.* **1979**, *18*, 1966.

(11) Beachley, O. T., Jr.; Tessier-Youngs, C. *Organometallics* **1983**, *2*, 796.

(12) Kovar, R. A.; Derr, H.; Brandau, D.; Callaway, J. O. *Inorg. Chem.* **1975**, *14*, 2809.

(13) Schmidbauer, H.; Findeiss, W. *Chem. Ber.* **1966**, *99*, 2187.