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Synthesis of Tris(pentamethylcyclopentadienyl)gallium(III)

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The previously unknown and elusive compound $Ga(C_5Me_5)_3$ has been prepared by several synthetic routes and has been characterized by elemental analyses and IR and ^1H NMR data. The compound has been prepared from $GaCl_3$ and excess $Na(C_5Me_5)$ in THF solution. A second general route to $Ga(C_5Me_5)_3$, the reaction of $Ga(C_5Me_5)_nCl_{3-n}$ (n = 1, 2) with sodium naphthalenide in THF solution, has also been realized. Heating of the product mixture at 50–60 °C under vacuum leads to the complete removal of the reaction solvent THF, an observation which suggests that $Ga(C_5Me_5)_3$ is a very weak Lewis acid. The title compound exists as a pentane- and ether-soluble colorless crystalline solid with a melting point of 168–170 °C.

Introduction

The study of cyclopentadienyl and pentamethylcyclopentadienyl compounds is part of our ongoing investigations of the chemistry of compounds of group 13 elements in typical and low oxidation states. The most generally useful synthetic route to the desired compounds utilizes metathetical reactions. The compound $Ga(C_5H_5)_3$ was prepared from $GaCl_3$ and excess LiC_5H_5 in diethyl ether.[1] An X-ray structural study revealed a molecule with a simple trigonal-planar gallium atom and cyclopentadienyl rings exhibiting η^1-coordination. In contrast, attempts to prepare $Ga(C_5Me_5)_3$ from $GaCl_3$ and $Li(C_5Me_5)$ proved futile as only $Ga(C_5Me_5)_2Cl$ was formed.[2] Regardless of the amount of excess $Li(C_5Me_5)$ used or whether Et_2O or THF was used as the solvent, the only gallium(III) product was $Ga(C_5Me_5)_2Cl$.

Cyclopentadienylindium(I) has also been readily prepared by a metathetical reaction[3] between InCl and LiC_5H_5. Similarly, $In(C_5Me_5)$ has been prepared and characterized by an X-ray structural study.[4] This new indium(I) compound exists as an apparent octahedral cluster with indium(I) atoms on the interior and η^5-pentamethylcyclopentadienyl groups on the exterior. Since no simple gallium(I) halogen compounds are available as starting materials for the possible preparation of organogallium(I) compounds by metathesis reactions, reduction reactions of organogallium(III) halogen compounds form the basis of a possible synthetic route. In this paper we report the results of our studies of reduction reactions of $Ga(C_5Me_5)Cl_2$ and $Ga(C_5Me_5)_2Cl$ using sodium naphthalenide in THF solution. The isolable products from these reactions are $Ga(C_5Me_5)_3$, naphthalene, and an insoluble gray solid indicative of gallium metal and sodium chloride.

Tris(pentamethylcyclopentadienyl)gallium(III) has also been independently prepared from $GaCl_3$ and excess $Na(C_5Me_5)$ in THF solution.

Experimental Section

General Data. All compounds described in this investigation were extremely sensitive to oxygen and moisture and were manipulated in a standard vacuum line or a purified argon atmosphere. The starting materials $Ga(C_5Me_5)_2Cl$ and $Ga(C_5Me_5)Cl_2$ were prepared as previously described.[2] The solvents were purified by conventional means (THF-refluxing Na/benzophenone) and were distilled immediately prior to use. 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 Model 683 spectrometer. Absorption intensities are reported with abbreviations w (weak), m (medium), s (strong), vs (very strong), and sh (shoulder). The ^1H NMR spectra were recorded at 90 MHz by using a Varian Model EM-390 spectrometer. Chemical shifts are reported in δ units (ppm) and are referenced to $SiMe_4$ as δ 0.00 and benzene as δ 7.13.

Preparation of $Na(C_5Me_5)$. Finely divided sodium (1.02 g, 44.3 mmol), which had been isolated by removing the toluene from a 30% Na/toluene dispersion by vacuum distillation, was combined neat with 5.41 g (39.7 mmol) of C_5Me_5H in a reaction tube in an Ar-filled drybox. Upon mixing, an exothermic reaction occurred and vigorous bubbling was observed. After removal of the reaction tube from the drybox, solvent (THF, 30 mL) was vacuum distilled into the reaction tube. The mixture was then stirred for 4 h at 60–80 °C to ensure complete reaction, although lack of further hydrogen evolution showed that the reaction had gone to completion in the drybox in the absence of solvent. After attempts to remove excess sodium dispersion from the THF solution of $Na(C_5Me_5)$ by filtration proved unsuccessful due to clogging of the frit by the finely divided sodium, the supernatant brown solution was carefully pipetted away from the fine gray sodium powder. A final filtration gave a clear brown solution from which THF was removed by vacuum distillation. The resulting brown solid was washed twice with 25 mL of pentane to remove a yellow, pentane-soluble oil from the insoluble, brown product $Na(C_5Me_5)$. Complete removal of THF from the product was ensured by evacuation overnight at 75–80 °C. The isolated yield of purified $Na(C_5Me_5)$ was 1.6 g (10 mmol, 25% yield).

$Na(C_5Me_5)$: ^1H NMR (THF-d_8 solution, δ) 1.94 (s); IR (Nujol mull, cm^{-1}) 2727 (s), 2671 (w, sh), 1580 (m, br), 1257 (m), 1150 (m), 1110 (m, sh), 1079 (m, br), 1043 (m, sh), 1012 (m, sh), 910 (w, sh), 870 (vw), 800 (w, sh), 787 (w), 762 (vw), 735 (w, sh), 716 (w), 640 (vw), 458 (vw), 397 (w), 328 (vs), 270 (m, sh).

Preparation of $Ga(C_5Me_5)_3$. A solution of 0.536 g (3.04 mmol) of freshly sublimed $GaCl_3$ in 40 mL of THF was added with stirring at room temperature to a THF (40-mL) solution of $Na(C_5Me_5)$ (1.540 g, 9.733 mmol). The reaction mixture was stirred at room temperature overnight, and the THF was completely removed, first by vacuum distillation and then by evacuating the system at 50–60 °c for 2 h. Pentane (70 mL) was vacuum distilled onto the products, and the mixture was filtered to separate a yellow solution of $Ga(C_5Me_5)_3$ from solid NaCl and unreacted $Na(C_5Me_5)$. Removal of the pentane by vacuum distillation left 0.742 g (1.56 mmol, 51.3% yield) of impure $Ga(C_5Me_5)_3$ as a yellow solid. Further purification was possible by washing the product with 5-mL portions of very cold (about −78 °C) pentane. However, this process reduced the yield of pure $Ga(C_5Me_5)_3$ to 0.400 g (0.841 mmol, 27.7% yield). Colorless crystals of $Ga(C_5Me_5)_3$ for a possible X-ray structural study were grown by slow sublimation of a sample of $Ga(C_5Me_5)_3$ in an evacuated sealed tube at 100–105 °C.

$Ga(C_5Me_5)_3$: colorless solid; mp 168–170 °C, melts to a yellow liquid; ^1H NMR (benzene solution, δ) 1.73; IR (Nujol mull, cm^{-1}) 2720 (m), 1613 (m), 1300 (w, sh), 1236 (vs), 1136 (m), 1125 (m), 1052 (m), 1042 (m, sh), 968 (w, sh), 940 (m), 815 (m), 786 (m), 716 (w, sh), 698 (vs), 685 (m, sh), 644 (w), 592 (m), 560 (m), 518

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(w), 412 (s), 292 (vs), 270 (m), 210 (m).

Reaction of $Ga(C_5Me_5)_2Cl$ with Na/Naphthalene. A solution of 3.0 mmol of sodium naphthalenide in 40 mL of THF was added at −78 °C to a solution of 1.127 g (3.00 mmol) of $Ga(C_5Me_5)_2Cl$ in 35 mL of THF. After the solution was stirred at −78 °C for 30 min and then at room temperature for 1 h, the THF was removed and 50 mL of pentane was added by vacuum distillation. The mixture was filtered to separate a gray precipitate from a light yellow solution. After removal of pentane, 0.240 g of a gray precipitate, indicative of gallium metal plus NaCl (97.9% yield), was isolated. The pentane-soluble, yellow solid was evacuated at 70–80 °C overnight to ensure quantitative removal of naphthalene and then washed several times with 5-mL portions of cold (about −78 °C) pentane to yield 0.310 g (0.652 mmol, 32.6% yield) of $Ga(C_5Me_5)_3$. The identity of the product was confirmed by its mp (165–170 °C), ^1H NMR and IR spectroscopic data, and C, H analyses (Calcd: C, 75.79; H, 9.54. Found: C, 75.98; H, 9.75).

Reaction of $Ga(C_5Me_5)Cl_2$ with Na/Naphthalene. A solution of 2.62 mmol of sodium naphthalenide in 50 mL of THF was added at −78 °C to a solution containing 0.360 g (1.31 mmol) of $Ga(C_5Me_5)Cl_2$ in 25 mL of THF. After being stirred for 1 h at −78 °C, the mixture was warmed to room temperature and the THF was removed by vacuum distillation. Then, 50 mL of pentane was added to the reaction mixture. Filtration and removal of pentane produced 0.185 g of a gray insoluble solid, indicative of gallium metal and NaCl (86.4% yield). The pentane-soluble material was a pasty, yellow solid which was evacuated overnight at 60 °C to ensure quantitative removal of naphthalene. The resulting material was shown to be slightly impure $Ga(C_5Me_5)_3$ by comparison of its melting point (148–161 °C), ^1H NMR, and IR spectroscopic data of that with known samples of $Ga(C_5Me_5)_3$. Qualitative analysis tests showed the lack of a AgCl precipitate when the gallium-containing product reacted with HNO_3 and $AgNO_3$, as well as the absence of sodium as indicated by a flame test.

Reaction of $Ga(C_5Me_5)_3$ with Na/Naphthalene. A solution of sodium naphthalenide (1.04 mmol in 25 mL of THF) was added at −20 °C to a solution containing 0.247 g (0.520 mmol) of $Ga(C_5Me_5)_3$ in 25 mL of THF. A black precipitate formed immediately upon mixing. The mixture was stirred for 3 h at room temperature and filtered, and then the THF was removed by vacuum distillation. The THF-soluble solid was evacuated overnight at 65 °C to ensure quantitative removal of naphthalene and then was washed six times with 25-mL portions of pentane. After removal of pentane under vacuum, the remaining THF soluble, pentane insoluble solid was isolated and identified by ^1H NMR and IR spectroscopic data as $Na(C_5Me_5)$ (0.168 g, 1.06 mmol). The pentane-soluble solid was shown to be $Ga(C_5Me_5)_3$ by IR spectroscopic data.

Results and Discussion

The previously unknown and elusive compound $Ga(C_5Me_5)_3$ has been prepared from $GaCl_3$ and excess $Na(C_5Me_5)$ in THF solution and has been characterized by melting point, elemental analyses, and IR and ^1H NMR spectroscopic data.

$$GaCl_3 + 3Na(C_5Me_5) \xrightarrow{THF} Ga(C_5Me_5)_3 + 3NaCl \qquad (1)$$

Since the initial attempts[2] to prepare $Ga(C_5Me_5)_3$ from $GaCl_3$ and excess $Li(C_5Me_5)$ led to the formation of only $Ga(C_5Me_5)_2Cl$, experiments using the more reactive compound $Na(C_5Me_5)$ in THF were undertaken. The observation that $Na(C_5Me_5)$ can be used to prepare $Ga(C_5Me_5)_3$ whereas $Li(C_5Me_5)$ replaces only a maximum of two chlorine atoms on gallium suggests that the higher reactivity of $Na(C_5Me_5)$ might be related to its increased tendency to exist in solution as simple ionic species rather than associated molecules.[5] When $Ga(C_5Me_5)_3$ is initially isolated from the reaction mixture, it is contaminated by a yellow material. Most of the unknown yellow impurity can be removed by washing the product with cold (−78 °C) pentane. However, this process significantly lowers the yield of the final product. Additional purification can be achieved by sublimation at 100–105 °C. Colorless crystals of $Ga(C_5Me_5)_3$ have a well-defined, reversible melting point of 168–170 °C. The compound is soluble in aprotic solvents, and both diethyl ether and THF can be removed completely. These observations suggest that $Ga(C_5Me_5)_3$ is a very weak Lewis acid. It is also of interest that $Ga(C_5Me_5)_3$ has enhanced thermal stability compared to $Ga(C_5H_5)_3$, a compound[1] which decomposes at 45 °C. It is regrettable that single crystals of $Ga(C_5Me_5)_3$, which were grown by sublimation at 100–105 °C for an X-ray structural study, proved unsuitable.

The reactions of (pentamethylcyclopentadienyl)gallium(III) derivatives including $Ga(C_5Me_5)Cl_2$, $Ga(C_5Me_5)_2Cl$, and $Ga(C_5Me_5)_3$ with sodium naphthalenide have been investigated as possible routes to a low oxidation state gallium derivative. The pentamethylcyclopentadienyl ligand might be expected to be an ideal ligand for the stabilization of a low oxidation state gallium compound. Furthermore, alkali-metal reduction reactions have been used previously to prepare group 13 compounds which have been described as low oxidation state compounds. The reduction of $AlEt_3$ using Na/naphthalene[6] has been reported to yield $NaAlEt_2$·naphthalene. The reaction of i-Bu_2AlCl with potassium pellets[7,8] in hexane yields $Al_2(i\text{-}Bu)_4$, a species with an apparent Al–Al bond. A related reaction to form $K_2Al_2(i\text{-}Bu)_6$ has also been reported.[9] In gallium chemistry, $Na_2Ga_2Me_6$ has been described as the initial product[10] from a $GaMe_3$–Na reaction in liquid NH_3. Similarly, the reaction[10] of $GaMe_2Cl$ with Na in liquid NH_3 has been reported to produce $(Me_2GaNH_2)_2$, NaCl, and H_2.

In the (pentamethylcyclopentadienyl)gallium(III)–sodium naphthalenide reactions the only isolated gallium products were $Ga(C_5Me_5)_3$ and gallium metal. When $Ga(C_5Me_5)Cl_2$ was reacted with $Na/C_{10}H_8$ in a 0.50 mol ratio, an insoluble gray solid consistent with an 86% yield (based on sodium) of NaCl and gallium metal was isolated (eq 2).

$$Ga(C_5Me_5)Cl_2 + 2Na/C_{10}H_8 \xrightarrow{THF} {}^1/_3Ga(C_5Me_5)_3 + {}^2/_3Ga^0 + 2NaCl + 2C_{10}H_8 \qquad (2)$$

The identity of the product as $Ga(C_5Me_5)_3$ was verified by a comparison of the melting point and ^1H NMR and IR spectral data with those of the known compound. The reaction of $Ga(C_5Me_5)_2Cl$ (eq 3) occurred similarly. When

$$Ga(C_5Me_5)_2Cl + Na/C_{10}H_8 \xrightarrow{THF} {}^2/_3Ga(C_5Me_5)_3 + {}^1/_3Ga^0 + NaCl + C_{10}H_8 \qquad (3)$$

$Ga(C_5Me_5)_3$ was reacted with $Na/C_{10}H_8$ in a 0.50 mol ratio (eq 4), the products were gallium metal and $Na(C_5Me_5)$.

$$Ga(C_5Me_5)_3 + 2Na/C_{10}H_8 \xrightarrow{THF} {}^1/_3Ga(C_5Me_5)_3 + {}^2/_3Ga^0 + 2Na(C_5Me_5) + C_{10}H_8 \qquad (4)$$

It is of interest that $NaGa(C_5Me_5)_4$ is not formed. Apparently, the steric bulk of the C_5Me_5 ligand reduces either the Lewis acidity of $Ga(C_5Me_5)_3$ or the Lewis basicity of $C_5Me_5^-$ to preclude the formation of $NaGa(C_5Me_5)_4$. Thus, the reactions of $Ga(C_5Me_5)_nCl_{3-n}$ (n = 3, 2, 1) with Na/naphthalene occur as previously observed for other group

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13 alkyl halide–sodium reactions except that MR_3 is formed instead of $NaMR_4$ when excess sodium is used. Additional reactions will have to be investigated for us to realize the successful synthesis of an organogallium(I) derivative.

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Registry No. $Ga(C_5Me_5)_3$, 105121-75-3; $Na(C_5Me_5)$, 40585-51-1; $Ga(C_5Me_5)_2Cl$, 105121-76-4; $Ga(C_5Me_5)Cl_2$, 105139-46-6; $GaCl_3$, 13450-90-3; C_5Me_5H, 4045-44-7.

Molecular Orbital Study of Olefin Homologation by Bimetallic Complexes. 1. The C–C Bond Formation Step

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A molecular orbital analysis of the formation of the metallacyclopentane $Fe_2(CO)_8C_3H_8$ from the bimetallic carbenic complex $Fe_2(CO)_8CH_2$ and ethylene (C_2H_4) is presented. Various mono-, di-, and tribridged isomers of the complexes $Fe_2(CO)_8C_3H_8$ and $Fe_2(CO)_8CH_2$ are considered. Two types of reaction paths have been studied. The first one is a two-step process. It involves the precoordination of C_2H_4 before the so-called insertion occurs. The second one is the direct insertion of C_2H_4 into the carbene–metal bond with or without a previous opening of the bridging structure. From the present study that is based on extended Hückel calculations, the direct insertion is the favored reaction path. The differences of regioselectivity experimentally observed for mono- and tribridged complexes are rationalized within this model.

I. Introduction

The formation of the C–C bond over heterogeneous transition-metal catalysts is an active field of fundamental research due to its major importance in industrial synthesis.[1] In recent years, several experimental studies helped in the understanding of its still obscure mechanism. In 1980–1981, Brady and Pettit[2] showed that CH_2N_2/H_2 or CO/H_2 maintained in identical temperature and pressure conditions over Fischer–Tropsch catalysts gives identical distributions of hydrocarbon products. In the same conditions, results favor the classical Fischer–Tropsch proposal[3] for the C–C bond formation mechanism in which metallic carbene surface species are involved. They are inconsistent with the two other major alternatives proposed on the one hand by Anderson and Emmet[4] (condensation between hydroxymethylene groups) and on the other hand by Pichler and Schlutz[5] (insertion of CO into a metal–alkyl bond). In 1983–1984, Basset et al.[6] and Strehlow et al.[7] showed that, over the same Fischer–Tropsch catalysts, a C_n olefin is homologated to higher C_{n+p} and lower C_{n-p} parent hydrocarbons (p = 1, 2, ...). They suggested that the homologation of olefin and Fischer–Tropsch reactions proceed by the same elementary step of C–C bond formation. Further, they have shown that the homologation is a C_1 addition step. These studies confirmed the role played by the carbene intermediate on the metallic surfaces in C–C bond formation. With the assumption of carbene involvement, two mechanisms have been considered.[6] The first one is a carbene insertion into a metal–alkyl bond; the second one is a coupling of carbene and olefins to yield metallacycles with three carbon atoms. The latter hypothesis is supported by the findings of Pettit[7] and Norton[8] which showed that the homologation of ethylene and propene into propene and butene, respectively, is made over bimetallic complexes of osmium and iron. In the case of osmium, a metallacyclopentane complex has been isolated.[8] The fact that identical distributions of products are obtained over various heterogeneous and bimetallic catalysts of C–C bond formation with various feed composition (C_2N_2/H_2, CO/H_2, C_2H_{2n}/H_2) suggests that all the catalysts involve a common mechanism with a metallacyclopentane intermediate. The present study intends to analyze the electronic factors that govern such a mechanism on the basis of molecular orbital considerations supported by extended Hückel technique (EHT) calculations.[9] Quantitative thermodynamic values for the reactions cannot be obtained since this method is unsuitable to give reliable determination of energetics in problems involving large structure reorganization. However, the trends we observe and the reasons behind them that are based on orbitals considerations remain valuable

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