aldehyde. In a reaction conducted to test the competitive rates of the acyl compound with EtOH and with $HCo(CO)_4$, an ether solution of the acyl was treated with a solution containing equimolar quantities of $HCo(CO)_4$ and EtOH. After 45 min at 23 °C, a 69% yield of hexanal and a 10% yield of ester were obtained (GLC). Obviously the acyl reacts faster with $HCo(CO)_4$ than with EtOH. Usually, when the ester is the desired product, the reaction is run in the presence of a base such as an amine.[12] Because of our knowledge of the second-order rate constants for reactions of $HCo(CO)_4$ with the acylcobalt tetracarbonyl and with 1,1-diphenylethylene,[13] it was of interest to conduct reaction 7 in the presence of $Ph_2C{=}CH_2$. When 1 mmol of diphenylethylene was added to 2 mmol of the acyl and 2 mmol of EtOH, 0.39 mmol of Ph_2CHCH_3 (78% yield) was obtained. The yield of ester was 1.32 mmol (66%), and less than 5% aldehyde was formed. When reaction 7 was carried out in the prescence of 1-pentene, relatively little hydroformylation of the pentene was observed. The relative rate of reaction with $HCo(CO)_4$ is therefore $Ar_2C{=}CH_2 > RCOCo(CO)_4 \gg RCH{=}CH_2$.

Reactions of aryl-substituted ethylenes with $HCo(CO)_4$ are known to proceed by a free radical mechanism, and in most of these reactions an inverse isotope effect is observed.[14] These reactions involve a radical pair intermediate formed in an endothermic reaction. The rate-determining step in the acylcobalt reaction is eq 5 which is clearly an exothermic reaction. Accordingly we anticipated a normal isotope effect in the reaction and indeed found $k[HCo(CO)_4]/k[DCo(CO)_4] = 3.6$.

Experimental Section

Preparation of $NaCo(CO)_4$, $CH_3(CH_2)_4COCo(CO)_4$, and $HCo(CO)_4$. $Co_2(CO)_8$ (1.72 g) was added to an excess 1% Na amalgam suspended in 60 mL of dry ether under CO. After being stirred for about 12 h, the solution was colorless and the IR spectrum[15] showed that the only cobalt species present was $Co(CO)_4^-$ (1886 cm^{-1}).

A portion of the ether solution of $NaCo(CO)_4$ was evaporated to dryness and the residue weighed (390 mg, 2 mmol) and dissolved in the appropriate solvent. The stoichiometric quantity of hexanoyl chloride in the same solvent was added at 0 °C under CO. The reaction was followed by disappearance of the 1886-cm^{-1} band. In ether, NaCl deposited and a yellow solution of $CH_3(CH_2)_4COCo(CO)_4$ was formed. In other solvents the solution was red probably due to some decomposition to octacarbonyl (IR).

$HCo(CO)_4$ was prepared according to the standard pyridine H_2SO_4 method.[16] $DCo(CO)_4$ was prepared by D_2O exchange.[17]

Kinetic Experiments. Rates were obtained by measuring the appearance of hexanal (GLC, 15% SE 30, 14 ft, 110 °C, He, 60 mL min^{-1}). *p*-Xylene was used as an internal standard.

In a typical experiment, a solution of $HCo(CO)_4$ was syringed into an equimolar solution of the acyl compound in a closed system under CO. The total volume was 24 mL. The solution was kept at room temperature (23 °C) and sampled periodically. Kinetic analysis of the data was done by standard procedures.[18]

Reactions of $CH_3(CH_2)_4COCo(CO)_4$ with EtOH in the Presence of $Ph_2C{=}CH_2$. To an ether solution of the acyl (2 mmol) was added a solution of $Ph_2C{=}CH_2$ (1 mmol) in EtOH (2 mmol). The reaction was stirred at 23 °C under CO, and samples were removed periodically for analysis (GLC).

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Registry No. $Me(CH_2)_4COCo(CO)_4$, 16126-65-1; $HCo(CO)_4$, 16842-03-8; $NaCo(CO)_4$, 14878-28-5; $Me(CH_2)_4COCl$, 142-61-0; $Ph_2C{=}CH_2$, 530-48-3; $CH_3(CH_2)_2CH{=}CH_2$, 109-67-1; EtOH, 64-17-5; D_2, 7782-39-0; $Co_2(CO)_8$, 10210-68-1.

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Synthesis and Reactions of $KGa(CH_2SiMe_3)_2H_2$ and an Attempted Preparation of $Ga(CH_2SiMe_3)_2H$. The Search for a Reductive Elimination Reaction

O. T. Beachley, Jr.,* and R. B. Hallock

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

Received June 20, 1983

The new compound $KGa(CH_2SiMe_3)_2H_2$ has been prepared from $Ga(CH_2SiMe_3)_2Br$ and excess KH and fully characterized by analysis and ^1H NMR and IR spectral data. The pure compound is thermally stable below 200 °C. Reaction of $KGa(CH_2SiMe_3)_2H_2$ with $Ga(CH_2SiMe_3)_2Br$ in benzene solution leads to the formation of $Ga(CH_2SiMe_3)_2H$, which readily decomposes at room temperature to gallium metal, H_2, and $Ga(CH_2SiMe_3)_3$. The experimental data suggest that $Ga(CH_2SiMe_3)_2H$ decomposes by an exchange process to form $Ga(CH_2SiMe_3)_3$ and unstable GaH_3. Reductive elimination does not appear to be an observed pathway to low oxidation state gallium compounds.

Introduction

The products from the reactions of $Ga(CH_2SiMe_3)_3$ and $In(CH_2SiMe_3)_3$ with KH in hydrocarbon solvents have been identified[1] as $KGa(CH_2SiMe_3)_3H$ and $KIn(CH_2SiMe_3)_3H$. These group 3 hydrido anions do not undergo simple reductive elimination reactions to form low oxidation state species and $SiMe_4$, as originally proposed.[2,3] Consequently, the synthesis of an organogallium(I) compound remains a formidable challenge. Since a reductive

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elimination reaction was considered to be a possible but little explored route to gallium(I), the nature and extent of the thermal stability of other organogallium(III) hydride derivatives were investigated. In this paper, the preparation, properteis, and reaction chemistry of $KGa(CH_2SiMe_3)_2H_2$ are described. The compound $KGa(CH_2SiMe_3)_2H_2$ has also been used for an attempted synthesis of $Ga(CH_2SiMe_3)_2H$. A neutral organogallium(III) hydride might undergo a reductive elimination reaction more readily than an anionic species. The hydrogen bound to gallium in a neutral molecule should have less partial negative charge than in an anionic species, a condition which might facilitate an apparent loss of a proton with concurrent reduction at gallium.

Results and Discussion

The compound $KGa(CH_2SiMe_3)_2H_2$ has been prepared from $Ga(CH_2SiMe_3)_2Br$[4] and a threefold excess of KH in dimethoxyethane.

$$Ga(CH_2SiMe_3)_2Br + 2KH(s) \xrightarrow[25\ °C]{DME} KGa(CH_2SiMe_3)_2H_2 + KBr(s) \quad (1)$$

No $SiMe_4$ was observed to be formed in the preparative reaction. The organohydridogallium(III) product was readily separated from excess KH and KBr by extraction with benzene. The last amounts of dimethoxyethane were then removed completely from the final product by continuous vacuum distillation at 65 °C. The identity of the final compound as $KGa(CH_2SiMe_3)_2H_2$ was confirmed by a quantitative hydrolysis study in 6 M HCl for 7 days at a bath temperature of 110–115 °C. The compound melts at 147–153 °C to a clear liquid. Then, the liquid can be cooled and remelted at the same temperature. Thermal decomposition does not appear to begin until a temperature of about 210 °C is reached. Thus, the pure compounds $KGa(CH_2SiMe_3)_3H$[1], $KGa(CH_2SiMe_3)_2H_2$, and $KGaH_4$[5] show similar but high thermal stability with no signs of decomposition or reductive elimination reactions below 200 °C.

The infrared spectra of $KGa(CH_2SiMe_3)_2H_2$ and $KGa(CH_2SiMe_3)_2D_2$ have been compared in order to identify the bands associated with the gallium hydrogen stretching modes. The spectrum of $KGa(CH_2SiMe_3)_2H_2$ exhibits a very strong, broad band centered at 1620 cm^{-1}, which is not present in a spectrum of $KGa(CH_2SiMe_3)_2D_2$. The ν(Ga–D) occurs at 1170 cm^{-1}. Thus, the Ga–H band at 1620 cm^{-1} is clearly visible in the spectrum, and it is not hidden[1] by Nujol as was the case for ν(Ga–H) in $KGa(CH_2SiMe_3)_3H$. The observation[1] that the infrared spectrum of $KGa(CH_2SiMe_3)_3H$ does not exhibit a band at 1620 cm^{-1} confirms that $KGa(CH_2SiMe_3)_2H_2$ was not an observable impurity, either after its initial preparation or after heating a sample as a benzene solution[1] for 5 days at a bath temperature of 105–110 °C and reisolating the solute. Thus, $KGa(CH_2SiMe_3)_3H$ does not appear to readily undergo disproportionation by dissociative or exchange reactions to form observable amounts of $KGa(CH_2SiMe_3)_2H_2$ in benzene solution. Organoboron hydride anions are also believed to be perfectly stable toward disproportionation in the absence of a catalyst,[6] a Lewis acid, but they are characterized by rapid hydride abstraction reactions[7] with reagents such as $H_3B{\cdot}THF$. Thus, attempts[6] to prepare $LiRBH_3$ from LiR and $H_3B{\cdot}THF$ produced product mixtures of $LiBR_{4-n}H_n$.

In contrast to the apparent stability of $KGa(CH_2SiMe_3)_3H$ to disproportionation, ^1H NMR spectral data for benzene solutions of $KGa(CH_2SiMe_3)_2H_2$ suggest that disproportionation or exchange reactions occur readily. The initial spectrum of a freshly prepared benzene solution of $KGa(CH_2SiMe_3)_2H_2$ exhibited only two lines at +0.34 ($SiMe_3$) and −0.80 (CH_2). Upon standing at room temperature for several days, two new lines at +0.26 and −0.91 gradually appeared. After longer time, the ^1H NMR spectrum did not change significantly but a very small amount of a colorless precipitate was observed. The similarity between the chemical shifts of the new lines and those observed[1] for $KGa(CH_2SiMe_3)_3H$, +0.31 ($SiMe_3$) and −0.91 (CH_2), suggest the occurrence of a disproportionation reaction. The simplest possibility is shown in eq 2 with the observed colorless precipitate being $KGa(CH_2SiMe_3)H_3$, an unknown compound. Another possible benzene-insoluble product would be $KGaH_4$. However, no attempt has been made to chemically identify the precipitate.

$$2KGa(CH_2SiMe_3)_2H_2 \rightleftarrows KGa(CH_2SiMe_3)_3H + KGa(CH_2SiMe_3)H_3 \quad (2)$$

The reaction of $KGa(CH_2SiMe_3)_2H_2$ with $Ga(CH_2SiMe_3)_2Br$ in benzene solution has been investigated in an attempt to prepare $Ga(CH_2SiMe_3)_2H$ and to study its decomposition and/or reduction pathways. The formation of $SiMe_4$ from decomposition would be consistent with a reductive elimination reaction, possibly by a concerted process. However, the formation of H_2 would suggest disproportionation by ligand exchange to form unstable GaH_3 and $Ga(CH_2SiMe_3)_3$ and/or radical reactions. Upon mixing the reagents $KGa(CH_2SiMe_3)_2H_2$ and $Ga(CH_2SiMe_3)_2Br$, a colorless precipitate (KBr) formed immediately. Then, the reaction mixture turned gray with evolution of H_2 upon standing at room temperature for a few hours. The isolated products included KBr, H_2, gallium metal, and $Ga(CH_2SiMe_3)_3$. Less than 0.01 mol of $SiMe_4$/mol of reagent was separated from the reaction mixture. All experimental observations are consistent with the hypothesis that $Ga(CH_2SiMe_3)_2H$ is the initial product. However, this gallium hydride is apparently unstable at room temperature and disproportionates to form $Ga(CH_2SiMe_3)_3$ and GaH_3, which then decomposes to gallium metal and hydrogen.[8] Our results show that $Ga(CH_2SiMe_3)_2H$ does not undergo a reductive elimination reaction to form $SiMe_4$ and $GaCH_2SiMe_3$ which then disproportionates to gallium metal and $Ga(CH_2SiMe_3)_3$. It is of interest that attempts[9] to prepare $In[CH(SiMe_3)_2]$ from InCl and the lithium alkyl led to the isolation of In, $H_2C(SiMe_3)_2$, and $[CH(SiMe_3)_2]_2$. The indium(III) alkyl $In[CH(SiMe_3)_2]_3$ was not observed. The ligand exchange processes for $Ga(CH_2SiMe_3)_2H$ are apparently signficantly faster than a reductive elimination reaction. The only other allkylgallium hydride described in the literature, $Ga(C_2H_5)_2H$, also decomposes[10] to form Ga, $Ga(C_2H_5)_3$, and H_2. All of these results are consistent with our earlier hypothesis[1] that $In(CH_2SiMe_3)_2H$ was formed during the decomposition of $KIn(CH_2SiMe_3)_3H$ but ligand exchange processes were faster than reduction. Thus, we conclude that a reductive elimination reaction of an organo group

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3 hydride probably will not be a useful route for the preparation of a low oxidation state group 3 derivative. Reductive elimination reactions of group 4 hydrides (R_3MH, M = Ge, Sn, Pb) are not synthetically useful routes to low oxidation state group 4 compounds[11] either.

Experimental Section

General Comments. All compounds described in this investigation were extremely oxygen and moisture sensitive and were manipulated in a vacuum line or in a purified argon atmosphere. All solvents were rigorously dried and vacuum distilled just prior to use. Infrared spectra were obtained by using a Perkin-Elmer 683 infrared spectrometer. The spectra were recorded as Nujol mulls by using CsI plates. (Bands due to Nujol have been omitted from data.) Proton NMR spectra were recorded by using a Varian EM-390 spectrometer. Proton chemical shifts are reported in δ units, parts per million downfield from tetramethylsilane, with benzene as an internal reference (δ 7.13). The solvent was vacuum distilled onto samples at −196 °C. Spectra were recorded immediately upon warming samples to room temperature unless stated otherwise.

$SiMe_4$ formed during synthetic, hydrolysis, and thermal decomposition reactions was separated by vacuum distillation with passage through two −78 °C traps and into a −196 °C trap and was measured by PVT or mass measurements. The purity of the $SiMe_4$ was determined by its ^1H NMR spectrum. Hydrogen was isolated and measured with a Toepler pump–gas burette assembly.

Synthesis and Characterization of $KGa(CH_2SiMe_3)_2H_2$. The reagents, 3.000 g (9.265 mmol) of $Ga(CH_2SiMe_3)_2Br$[4] and 1.115 g (27.80 mmol) of KH, were combined in a reaction tube equipped with a Teflon valve in the drybox. Then, 20 mL of dry dimethoxyethane was vacuum distilled into the tube. After 4-h reaction time at room temperature, the dimethoxyethane and a trace of noncondensable gas were removed on the vacuum line. Then, the mixture was extracted with dry benzene. The filtrate, a white paste, was pumped on overnight at 65 °C to remove all dimethoxyethane. Since the product was gray, the mixture was extracted with benzene a second time and then washed twice with cold *n*-pentane. The resulting colorless solid (1.21 g, 4.25 mmol) $KGa(CH_2SiMe_3)_2H_2$, which was slightly soluble in cold C_5H_{12}, was isolated in 45.8% yield based on $Ga(CH_2SiMe_3)_2Br$. $KGa(CH_2SiMe_3)_2H_2$: mp 147–153 °C, bubbles and turns gray 212 °C; hydrolysis (6 M HCl, 110 °C, 7 days) of 0.288 g (1.01 mmol) yields 1.99 mmol of H_2 and 1.98 mmol of $SiMe_4$ (by PVT measurements); ^1H NMR (C_6H_6, ppm, reference C_6H_6 7.13); spectrum immediately upon dissolution, +0.34 (s, 4.3, Me), −0.80 (s, 1.0, CH_2), spectrum after 4 months +0.33 (s, 10.2, Me), +0.26 (s, 4.0, Me), −0.81 (s, 1.9, CH_2), −0.91 (s, 1.0, CH_2). IR (Nujol Mull): 1620 (vs, br), 1290 (w), 1253 (m), 1239 (s), 960 (s), 850 (vs), 820 (vs), 775 (s), 746 (s), 715 (m), 700 (m), 679 (m), 604 (w), 575 (m), 511 (m), 479 (vw), 442 (w), 250 (vw) cm^{-1}. $KGa(CH_2SiMe_3)_2D_2$: ^1H NMR (C_6H_6, ppm, reference C_6H_6 7.13) spectrum immediately upon dissolution, +0.33 (s, 4.0, Me), −0.82 (s, 1.0, CH_2), after 24 h, +0.33 (s, 11.1, Me), +0.26 (s, 3.9, Me), −0.82 (s, 2.1, CH_2), −0.92 (s, 1.0, CH_2); IR (Nujol mull) 1650 (w, br), 1290 (vw), 1251 (m), 1238 (s), 1170 (m, br), 955 (vs), 849 (vs), 819 (vs), 742 (m), 714 (m), 677 (w), 600 (m), 585 (w, sh), 514 (m), 482 (vw) cm^{-1}.

Reaction of $KGa(CH_2SiMe_3)_2H_2$ with $Ga(CH_2SiMe_3)_2Br$. An Attempted Synthesis of $Ga(CH_2SiMe_3)_2H$. To 0.381 g (1.34 mmol) of $KGa(CH_2SiMe_3)_2H_2$ in 5 mL of C_6H_6 was added 0.433 g (1.34 mmol) of $Ga(CH_2SiMe_3)_2Br$ in 5 mL of C_6H_6 at room temperature. A white precipitate formed immediately but turned gray after several hours. After being stirred for 24 h, the mixture was cooled to −196 °C and 1.10 mmol of H_2 were measured with a Toepler pump–gas burette assembly. Fractionation of the volatile components throught two −78 °C traps and into a −196 °C trap produced less than 0.01 mmol of $SiMe_4$ (PVT measurements). The mixture was then filtered to separate 0.210 g of a gray insoluble solid (KBr plus Ga). The removal of all benzene from the filtrate left a yellow paste. Vacuum distillation of this paste at a bath temperature of 110 °C produced 0.41 g (1.2 mmol) of $Ga(CH_2SiMe_3)_3$ which was identified by ^1H NMR (+0.13, C_6H_6) and IR.

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Registry No. $KGa(CH_2SiMe_3)_2H_2$, 87828-71-5; $Ga(CH_2SiMe_3)_2Br$, 74251-17-5; $Ga(CH_2SiMe_3)_2H$, 87801-07-8.

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Condensation of Mononuclear $[HM(CO)_4]^-$ to Trinuclear $[HM_3(CO)_{11}]^-$ Metal Hydrido Carbonyl Anions (M = Fe, Ru, Os) under Protic and Water Gas Shift Conditions

Jeffery C. Bricker, Nripendra Bhattacharyya, and Sheldon G. Shore*

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210

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Stoichiometries and conditions for the condensation of $[HM(CO)_4]^-$ to $[HM_3(CO)_{11}]^-$ for M = Fe, Ru, and Os have been determined. Under protic and water gas shift conditions, the $[HRu(CO)_4]^-$ anion is rapidly converted to the trinuclear cluster anion $[HRu_3(CO)_{11}{}^-]$. In protic media the $[HFe(CO)_4]^-$ anion condenses to $[HFe_3(CO)_{11}]^-$, but at a markedly slower rate. Under water gas shift conditions, $[HFe(CO)_4]^-$ does not form $([HFe_3(CO)_{11}]^-$. Instead, within a period of 24 h a catalytically inactive material is formed. In protic media $[HOs(CO)_4]^-$ slowly forms $[HOs_3(CO)_{11}]^-$. The $[HOs(CO)_4]^-$ anion is more active than $[HOs_3(CO)_{11}]^-$ for the catalysis of the water gas shift reaction.

Introduction

Minimal details have been reported concerning the abilities of mononuclear anions of the type $[HM(CO)_4]^-$ (M = Fe, Ru, Os) to form higher nuclearity cluster anions through self-condensation.[1-3] It is known, however, that these anions are stable in aprotic media and that $[HRu(CO)_4]^-$ is converted to $[HRu_3(CO)_{11}]^-$ in CH_3OH at 60 °C.[2] It is also known that the anion $[HFe(CO)_4]^-$ interconverts with $[HFe_3(CO)_{11}]^-$ in aqueous amine solutions in the

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