Journal of Organometallic Chemistry, 453 (1993) 7–12

JOM 23413

The reaction of hydrogallium(III) dichloride ($HGaCl_2$) with olefines, acetylenes, and α,β-unsaturated ketones

Joji Ohshita and Hubert Schmidbaur

Anorganisch-Chemisches Institut der Technischen Universität München, Lichtenbergstrasse 4, W-8046 Garching (Germany)

(Received November 13, 1992)

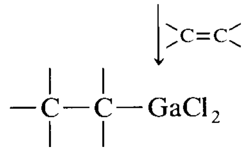
Abstract

The reaction of $HGaCl_2$ with 1-octene yields 1-octylgallium(III) dichloride in 77% yield, but with 2-octene a 2:1 mixture of 2- and 3-octylgallium dichloride(III) is obtained in 88% yield, and the reaction of (*E*)-stilbene gives an even more complex mixture. Hydrogallation of 1,4-diphenylbutadiene with $HGaCl_2$ followed by hydrolysis yields 1,4-diphenylbutane in 53% yield. The reactions of diphenylacetylene and 4-octyne under the same conditions give (*E*)-stilbene and (*E*)-4-octene in 76% and 63% yield, respectively, while 1-octyne undergoes polymerization. 2-Benzoylstyrene (calcone) reacts with $HGaCl_2$ to give, as the main product, a compound arising from 1,4-addition of the H–Ga bond across the enone system, together with a double hydrogallation product.

1. Introduction

The behaviour of hydroaluminium compounds, such as $LiAlH_4$ (LAH) and $i\text{-}Bu_2AlH$ (DIBAH), towards unsaturated hydrocarbons has been investigated in great detail and the usefulness of the "hydroalumination" reaction as a synthetic tool in organic chemistry is well documented [1]. However, much less attention has been focused on the interaction of hydrogallium compounds with unsaturated compounds [2,3]. Some years ago, as part of our continuous studies of organogallium compounds [4], we showed that the reaction of gallium(III) trichloride with trimethylsilane offered a convenient route to $HGaCl_2$, and that the hydrogallane thus prepared reacts readily with both terminal and internal olefines, and with acetylene, acetone, and acetonitrile, to give high yields of products arising from the addition of the H–Ga bond across the unsaturated bond [3]. In a previous paper, we also indicated some clear limitations of the hydrogallation, namely that the reactions with styrene, phenylacetylene, and 2,3-dimethyl-1,3-butadiene do not afford hydrogallation products but polymerization products [3a].

$$GaCl_3 + HSiMe_3 \longrightarrow HGaCl_2 + Me_3SiCl$$



$$\Big\downarrow {>}C{=}C{<} \qquad -\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-GaCl_2$$

To explore further the scope of the hydrogallation reaction of unsaturated compounds, we have investigated the reactions of $HGaCl_2$ with unsaturated compounds, including carefully selected olefines, acetylenes, and α,β-unsaturated ketones.

2. Results and discussion

2.1. Olefines

From the reaction of 1-octene with $HGaCl_2$ in CH_2Cl_2 at room temperature, 1-octylgallium dichloride (**1**) was obtained in 77% yield as the sole volatile product. Compound **1** was isolated by distillation and characterized by ^1H and ^{13}C NMR and mass spectrometric analyses, as well as by elemental analysis (see Experimental section). This reaction proceeds with

---

Correspondence to: Prof. Dr. H. Schmidbaur.

0022-328X/93/$6.00

remarkably high regioselectivity, no other regioisomers being detected by either ^1H or ^{13}C NMR spectrometric analysis of the reaction mixture.

$$(n\text{-}C_6H_{13})CH{=}CH_2 + HGaCl_2 \longrightarrow (n\text{-}C_8H_{17})GaCl_2 \qquad (\mathbf{1})$$

The analogous reaction with 2-octene, however, proceeds with much lower regioselectivity and gives a 2 : 1 mixture of 2- and 3-octylgallium(III) dichloride (**2** and **3**), in a total yield of 88%. The ratio of the products was determined from the integraly of the signals in the ^1H NMR spectrum.

$$(n\text{-}C_5H_{11})CH{=}CHCH_3 + HGaCl_2 \longrightarrow (n\text{-}C_5H_{11})CH_2CH(GaCl_2)CH_3 \qquad (\mathbf{2})$$

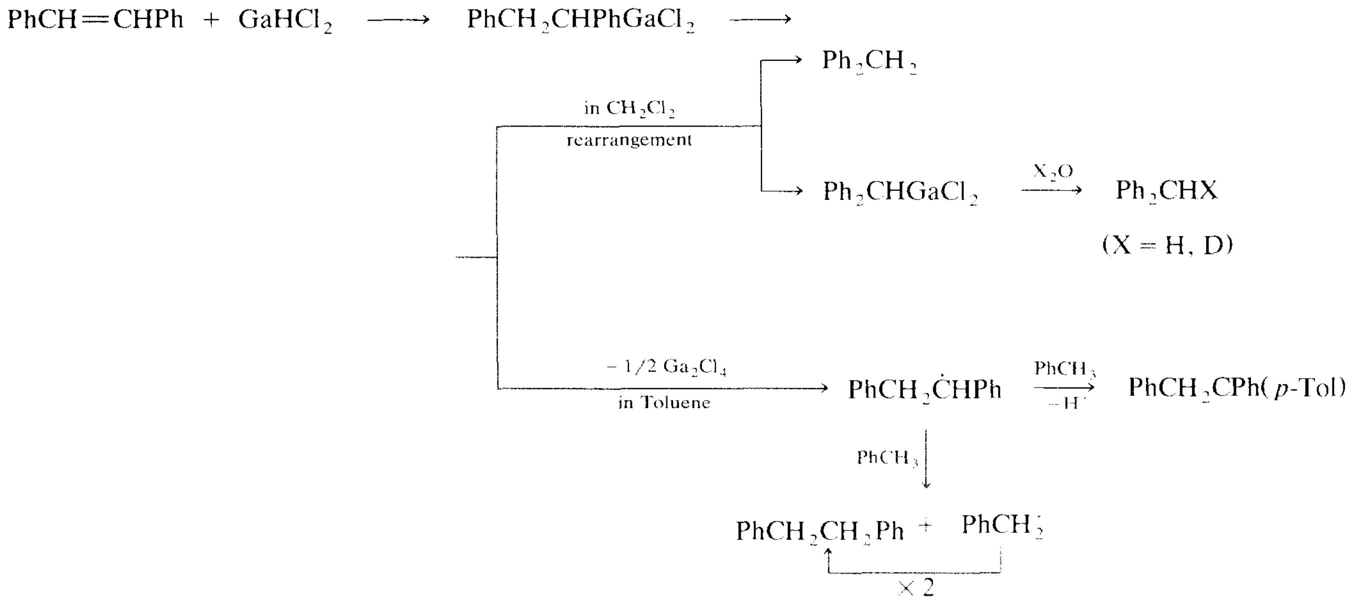
$$+ (n\text{-}C_5H_{11})CH(GaCl_2)CH_2CH_3 \qquad (\mathbf{3})$$

By contrast, the interaction of $HGaCl_2$ with (*E*)-stilbene in CH_2Cl_2 leads to a complex mixture of products. Attempts to characterize the compounds in the mixture by direct NMR studies were unsuccessful, and so the reaction mixture was hydrolyzed and the resulting mixture of hydrocarbons investigated by ^1H and ^{13}C NMR and GLC-MS, which revealed, very surprisingly, that the main volatile product was diphenylmethane, (*ca.* 11% yield), which was accompanied by traces of 1,2-diphenylacetylene and several unidentified volatiles (each in < 5% yield) and a large quantity of non-volatile species.

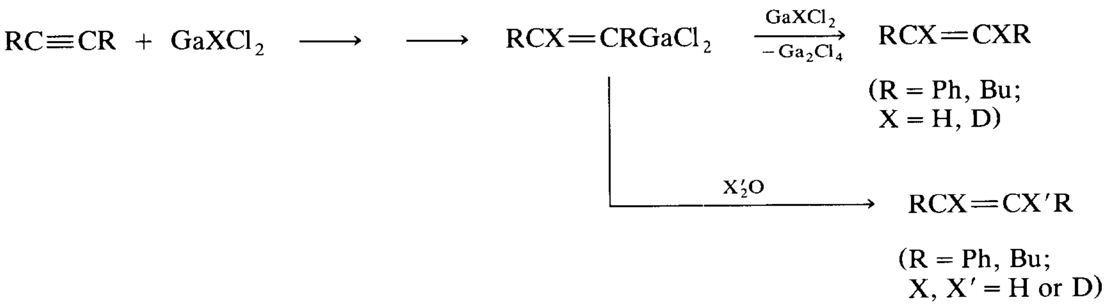
Treatment of the reaction mixture with D_2O gave diphenylmethane containing about 50% of deuterium in the methylene group (Ph_2CHD), along with traces of 1-D-1,2-diphenylethane.

When carried out in toluene the hydrogallation reaction is very slow at room temperature, but is rapid at 100°C, and hydrolysis of the reaction mixture affords 1,2-diphenylethane and 1,2-diphenyl-1-(*p*-tolyl)ethane in 38% and 24% yield, respectively. Contrary to expectation, quenching of the reaction mixture with D_2O gave only the same undeuterated products, indicating that these two compounds were produced before quenching.

Scheme 1 depicts a possible mechanism for the observed reaction. This mechanism involves the formation of an intermediate complex, 1,2-diphenylethylgallium(III) dichloride, produced from hydrogallation of (*E*)-stilbene. It is likely that in CH_2Cl_2 the intermediate undergoes a 1,2-shift of a phenyl group accompanied by C–C bond cleavage to generate the diphenylmethyl moieties. The course of the reaction in toluene at 100°C could be accounted for in terms of homolytic cleavaged of the C–Ga bond of the intermediate followed by aromatic substitution of toluene by the resulting diphenylethyl radical. Thermal homolytic cleavage of Ga–C bonds at 200°C has been reported previously [5]. A phenyl group attached to the α-carbon atom appears to favour the formation of radicals.



Scheme 1.



Scheme 2.

The reaction of 1,4-diphenyl-1,4-butadiene with $HGaCl_2$ proceeds in a quite different manner compared with that of 2,3-dimethyl-1,3-butadiene (which gives only non-volatile products [3a]). Hydrolysis of the reaction mixture gives a 54% yield of 1,4-diphenylbutane, as expected for a double hydrogallation reaction. Traces of 1,4-diphenylbutene derivatives and a large amount of non-volatile products are also present.

$$PhCH{=}CH{-}CH{=}CHPh + 2\,HGaCl_2 \longrightarrow \xrightarrow{H_2O} Ph(CH_2)_4Ph$$

2.2. Acetylenes

When diphenylacetylene is treated with $HGaCl_2$ in CH_2Cl_2 at room temperature, and this is followed by hydrolysis, (*E*)-stilbene is obtained in 76% yield as the sole volatile product. None of the (*Z*)-isomer, which would be the expected result of a *cis*-addition of the H–Ga bond to the triple bond, was detected in the reaction mixture by either GLC-MS or NMR spectroscopy. Attempted distillation to allow isolation of gallium-containing complexes before hydrolysis resulted in decomposition of the products. Decomposition of alkenylgallium complexes at elevated temperatures has been reported previously [2a].

When quenched with D_2O, the reaction mixture obtained from $HGaCl_2$ and diphenylacetylene yielded (*E*)-stilbene in 20% yield, together with the expected 1-D-(*E*)-stilbene (52% yield).

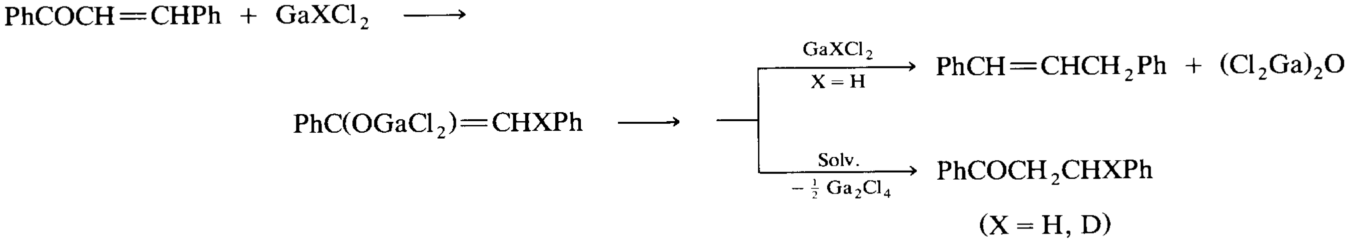
$$PhC{\equiv}CPh + GaHCl_2 \longrightarrow \xrightarrow{D_2O} PhCH{=}CDPh + PhCH{=}CHPh$$

The reaction of diphenylacetylene with deuteriogallium(III) dichloride ($DGaCl_2$) followed by hydrolysis gave 1-D-(*E*)-stilbene and 1,2-D_2-(*E*)-stilbene in 61 and 12% yield, respectively.

$$PhC{\equiv}CPh + GaDCl_2 \longrightarrow \xrightarrow{H_2O} PhCH{=}CDPh + PhCD{=}CDPh$$

These results clearly indicate that *ca.* 10–20% of the diphenylacetylene reacts with 2 equiv. of $HGaCl_2$ to form (*E*)-stilbene before hydrolysis (Scheme 2).

In order to obtain additional information about the gallium-containing intermediates, the progress of the reaction of $HGaCl_2$ with diphenylacetylene in CD_2Cl_2 was monitored by ^1H and ^{13}C NMR spectroscopy. After 8 h, the ^1H and ^{13}C NMR spectra of the reaction mixture showed the presence of (*E*)-stilbene in *ca.* 8% yield prior to hydrolysis. In addition to signals due to (*E*)-stilbene, the ^1H NMR spectrum showed two signals at 7.58 and 7.69 ppm assigned to an olefinic function, with an intensity ratio of *ca* 1:2, and the ^{13}C



Scheme 3.

NMR spectrum exhibited four signals at 139.6, 141.3, 145.6, and 146.1 ppm in the olefin region, and 16 signals in the region for arene carbon (see Experimental section). These signals are attributable to (*E*)-1-phenylstyryl- and (*Z*)-1-phenylstyrylgallium(III) dichloride. Indeed, upon hydrolysis of the reaction mixture, these signals disappeared completely and only signals ascribed to (*E*)-stilbene were observed in both the ^1H and the ^{13}C NMR spectra.

The reaction of 4-octyne under similar conditions, followed by hydrolysis, gave 4-(*E*)-octene in 63% yield as the sole volatile product. The lower yield compared to that of (*E*)-stilbene from diphenylacetylene results from the formation of a dimer (*ca.* 5% yield), which was detected in the reaction mixture by GLC-MS (m/e = 222). Monitoring the progress of the reaction by ^1H and ^{13}C NMR spectroscopy revealed the presence of 4-(*E*)-octenyl- and 4-(*Z*)-octenylgallium(III) dichloride and 4-(*E*)-octene in a ratio of 76 : 10 : 14 prior to hydrolysis (see Experimental section), and hydrolysis of the mixture converted these gallium-containing compounds completely into 4-(*E*)-octene.

In contrast, the interaction of $HGaCl_2$ with 1-octyne resulted in the formation of only non-volatile products even at −78°C, as in the case of the reaction of phenylacetylene reported previously [3a].

2.3. *α,β-Unsaturated ketones*

Standard hydroalumination of conjugated enone systems proceeds in the fashion of 1,2-addition [1]. By contrast, the reaction of calcone with $HGaCl_2$ followed by hydrolysis gave 1,3-diphenyl-1-propanone, which corresponds to a 1,4-hydrogallation of the enone system, in 30% yield. In this reaction, a double reduction product, 1,3-diphenylpropene, was also obtained, in 25% yield. Similar reactions were carried out in the presence of a Lewis-base in the hope that such a donor would reduce the reactivity of the hydrogallane, so leading to higher selectivity. As expected, the reaction in the presence of an equimolar amount of ether, pyridine, or triethylamine under the same conditions afforded only 1,3-diphenyl-1-propanone in 40–50% yield.

$$\mathrm{PhCOCH{=}CHPh} + \mathrm{HGaCl_2} \longrightarrow$$
$$\xrightarrow{H_2O} \mathrm{PhCOCH_2CH_2Ph} + \mathrm{PhCH{=}CHCH_2Ph}$$

However, similar interaction of 1-phenylbut-2-en-1-one with $HGaCl_2$ in CH_2Cl_2 gave a large amount of non-volatile products. No volatile products were obtained and 20% of the starting compound was recovered.

To learn more about the hydrogallation of calcone, we carried out the same reaction with $DGaCl_2$, followed by hydrolysis; 3-D-1,3-diphenylpropanone was obtained in 57% yield as the sole volatile product, indicating that the first step in the reaction is undoubtedly conjugated addition of the D–Ga bond across the enone unit. No double reduction product analogous to 1,3-diphenylpropene (above) was produced. On the other hand, deuteriolytic quenching (with D_2O) of the mixture obtained from the reaction of $HGaCl_2$ with calcone gave 1,3-diphenyl-1-propanone and 1,3-diphenylpropene, both in 22% yield. Careful NMR studies showed that no deuterium was incorporated into these products. Moreover, the ^1H and ^{13}C NMR spectra of the reaction mixture in CD_2Cl_2 showed the presence of 1,3-diphenyl-1-propanone and 1,3-diphenylpropene before hydrolysis. These facts clearly indicate that the product 1,3-diphenylpropene is not produced from hydrolysis of 1,3-diphenylpropanone, but from double hydrogallation of the starting calcone before hydrolysis. The formation of 1,3-diphenyl-1-propanone, probably involves hydrogen abstraction from any substrates present in the mixture. However, there is as yet no positive evidence to confirm this mechanism.

In conclusion, the results of the present study demonstrate that $HGaCl_2$ can react with aliphatic olefines, internal acetylenes, and calcone to give clean hydrogallation products in moderate yields. Hydrogallation of olefines with aryl substituents and terminal acetylenes both take a very different course, and further work is necessary to clarify the detailed mechanism.

3. Experimental section

3.1. *General*

All reactions were carried out under a slightly positive pressure of purified nitrogen. The CH_2Cl_2 and toluene used as solvents were distilled from P_2O_5 and sodium, respectively, and stored over molecular sieves until use. The $HGaCl_2$ was prepared from the stoichiometric reaction of gallium(III) trichloride and trimethylsilane, as described previously [3a]. After removal of the by-product, trimethylsilyl chloride, under reduced pressure, the residue was used without further purification. $DGaCl_2$ was prepared similarly by use of deuteriotrimethylsilane in place of trimethylsilane. All NMR spectra were recorded on a JEOL GX-400 spectrometer at ambient temperature with tetramethylsilane as internal standard. Mass spectra were obtained with Varian MAT112 and MAT311A spectrometers and a Hewlett Packard Model HP5970 system.

3.2. *1-Octylgallium(III) dichloride (1)*

To a mechanically stirred solution of $HGaCl_2$ (1.10 g, 7.78 mmol) in 10 ml of CH_2Cl_2, 1.20 ml (7.49 mmol) of 1-octene was added at room temperature. The mixture was stirred for 15 h at room temperature. The solvent was distilled off and the residue distilled under reduced pressure to give 1.47 g of 1-octylgallium(III) dichloride (77% yield), b.p. 105°C (1 mmHg). MS: *m/e* 217 ($M^+ - Cl$). ^1H NMR (in C_6D_6): δ 0.95 (t, 3H, $J = 6.84$ Hz, CH_3); 1.02 (t, 2H, $J = 7.32$ Hz, CH_2Ga); 1.25–1.34 (m, 10H, CH_2); 1.50 (brq, 2H, $J = 6.84$ Hz, CH_2). ^{13}C NMR (in C_6D_6): δ 14.3, 22.6 (br.), 23.0, 24.4, 29.3, 29.4, 32.1, 33.3. Anal. Found: C, 37.43; H, 7.15; Cl, 27.99. $C_8H_{17}GaCl_2$ calcd. (253.85): C, 37.85; H, 6.75; Cl, 27.93%.

3.3. 2- and 3-Octylgallium(III) dichloride (2) and (3)

As described for **1**, the reaction of 0.58 g (4.09 mmol) of $HGaCl_2$ and 0.63 ml (4.04 mmol) of 2-octene yielded a 2:1 mixture of 2- and 3-octylgallium(III) dichloride, b.p. 130–160°C (1 mmHg). ^1H NMR (in C_6D_6): δ 0.86 (br. t, 3H, $J = 6.91$ Hz, CH_3); 1.09 (brd, 1.3H, $J = 6.84$ Hz, $CH_3(CHGa)$); 1.16–1.55 (m, 13.7H, CH and CH_2). ^{13}C NMR (in C_6D_6): δ 14.17, 14.23, 14.4, 16.3, 22.7, 22.9, 24.3, 29.5, 29.9, 30.1, 30.9, 31.9, 32.1, 33.11, 33.12, 34.0. Anal. Found: C, 37.48; H, 6.60; Cl, 28.07. $C_8H_{17}GaCl_2$ calcd. (253.85): C, 37.85; H, 6.75; Cl, 27.93%.

3.4. Reaction of (E)-stilbene with $HGaCl_2$ in CH_2Cl_2

A mixture of 0.63 g (4.43 mmol) of $HGaCl_2$ and 0.80 g (4.44 mmol) of (*E*)-stilbene in 5 ml of CH_2Cl_2 was stirred for 15 h at room temperature and then hydrolyzed with 5 ml of distilled water. The organic layer was separated and the aqueous layer was extracted with 2 × 5 ml of CH_2Cl_2. The organic layer and the extracts were combined and dried over anhydrous magnesium sulfate. After evaporation of the solvent, Kugelrohr distillation of the residue gave 0.10 g of oil (boiling range 150–200°C (1 mmHg)), leaving 0.28 g of residue. The oil was analyzed by ^1H and ^{13}C NMR spectroscopy and GLC-MS, which showed the presence of diphenylmethane (*ca.* 11% yield) and traces of 1,2-diphenylethane in addition to many unidentified products (each in < 5% yield). Spectral data obtained for dimethyldiphenylmethane and 1,2-diphenylethane were identical with those for authentic samples.

3.5. Reaction of (E)-stilbene with $HGaCl_2$ in toluene

As described for the reaction in CH_2Cl_2, 0.34 g (2.22 mmol) of $HGaCl_2$ and 0.39 g (2.17 mmol) of (*E*)-stilbene in 5 ml of toluene was kept at 100°C, and subsequent hydrolysis and distillation gave 0.35 g of a 62:38 mixture of 1.2-diphenylethane and 1,2-diphenyl-1-(*p*-tolyl)ethane (boiling range 150–200°C (1 mmHg)). All spectral data obtained for 1,2-diphenylethane were identical with those for an authentic sample. 1,2-Diphenyl-1-(*p*-tolyl)ethane: MS: *m/e* 181 ($M^+ -$ Tol). ^1H NMR (in $CDCl_3$): δ 2.24 (s, 3H, CH_3); 3.32 (d, 2H, $J = 8.86$ Hz, CH_2); 4.19 (t, 1H, $J = 8.86$ Hz, CH); 7.02–7.32 (aryl protons overlapped by signals due to 1,2-diphenylethane). ^{13}C NMR (in $CDCl_3$): δ 37.8, 42.2, 52.6, 125.8, 126.0, 127.9, 128.0, 128.3, 128.4, 129.00, 129.03, 135.5, 140.4, 141.5, 144.7.

The hydrogallation of 1,4-diphenyl-1,3-butadiene, diphenylacetylene, 4-octyne, calcone, and 1-phenylbut-2-en-1-one were carried out as described for the reaction of (*E*)-stilbene in CH_2Cl_2 at room temperature. The products, (*E*)-stilbene and (*E*)-4-octene, were isolated by Kugelrohr distillation. In the reaction of diphenylacetylene with $HGaCl_2$ followed by deuterolysis, D_1-stilbene was obtained as a mixture with (*E*)-stilbene, and similar reaction with $DGaCl_2$ followed by hydrolysis gave a mixture of D_1-stilbene and D_2-stilbene. The ratios of these products were determined from the integrals of the resonances of the olefin protons and aryl protons in the ^1H NMR spectra. 1,4-Diphenylbutane was obtained as a mixture with traces of 1,4-diphenylbutene derivatives. 1,3-Diphenylpropanone and 1,3-diphenylpropene could not be separated and were analyzed as a mixture. All spectral data obtained for 1,4-diphenylbutane [6], 1,3-diphenylpropanone [7] and 1,3-diphenylpropene [8] were in good agreement with literature values.

3.6. Monitoring the reaction progress by NMR

A mixture of *ca.* 100 mg of a substrate and an equimolar amount of $HGaCl_2$ in 0.5 ml of CD_2Cl_2 was placed in a 5 mm NMR tube and the tube was sealed tightly. After 8 h the mixture was analyzed by ^1H and ^{13}C NMR spectroscopy, and shown to contain products as follows: (*E*)- and (*Z*)-1-phenylstyrylgallium(III) dichloride: ^1H NMR (in CD_2Cl_2): δ 7.34–7.44 (phenyl protons, overlapping with signals of (*E*)-stilbene); 7.38 (br, s, 0.33H, olefin proton); 7.69 (brs, 0.66H, olefin proton). ^{13}C NMR (in CD_2Cl_2): δ 126.8, 127.6, 127.8 (br, 2C), 127.86, 127.93, 127.9, 128.3, 128.4, 128.7, 128.8, 129.2, 129.4, 127.9, 128.3, 128.4, 128.7, 128.8, 129.2, 129.4, 129.5, 129.6, 131.9, 139.6, 141.3, 145.6, 146.1. (*E*)- and (*Z*)-4-octenylgallium(III) dichloride: ^1H NMR (in CD_2Cl_2): δ 0.87–2.03 (m, CH and CH_2); 6.04 (br, t, 0.12H, $J = 8.30$ Hz, olefin proton); 6.28 (br, t, $J = 7.32$ Hz, olefin proton). ^{13}C NMR (in CD_2Cl_2): δ 13.7–32.3, 130.8, 143.1, 146.0, 147.6.

Acknowledgements

This work was supported by Deutsche Forschungsmeinschaft and by Fonds der Chemischen Industrie. J. O. is indebted to the A. v. Humbold Foundation for a research fellowship.

References

1 (a) J. Mole and E.A. Jeffrey, *Organoaluminium Compounds*, Elsevier, Amsterdam, 1972; (b) P.A. Chaloner, in F.R. Hartley (ed.), *The Chemistry of the Metal-Carbon Bond*, Wiley, New York, 1987, Ch. 4.

2 (a) J.J. Eisch, *J. Am. Chem. Soc., 84* (1962) 3836; (b) H. Schumann, U. Hertmann and W. Wassermann, *Polyhedron, 9* (1990) 353; (c) K. W. Egger, *J. Chem. Soc. A*, (1971) 3603.

3 (a) H. Schmidbaur and H.F. Klein, *Chem. Ber., 100* (1967) 1129; (b) H. Schmidbaur and H.F. Klein, *Angew. Chem., 78* (1966) 306; *Angew. Chem., Int. Ed. Engl., 5* (1966) 312.

4 H. Schmidbaur, *Angew. Chem., 97* (1985) 893; *Angew. Chem., Int. Ed. Engl., 24* (1985) 893 and refs. therein.

5 (a) N.N. Travkin, B.G. Gribov, V.P. Rumyantseva, I.G. Tonoyan and E.N. Zorina, *J. Gen. Chem., USSR, 45* (1975) 303; (b) Y.A. Aleksandrov, G.I. Makin, O.N. Druzhkov, Y.Y. Baryshnikov, T.K. Postnikova and B.I. Kozyrkin, *J. Gen. Chem., USSR, 50* (1980) 2642.

6 M.A. Wilson, H. Rottendorf, P.J. Collin and A.M. Vassallo, *Aust. J. Chem., 37* (1984) 2379.

7 T. Kobayashi, H. Kawate, H. Kakiuchi and H. Kato, *Bull. Chem. Soc. Jpn., 63* (1990) 1937.

8 E.K. Raunio and W.M. Bonner, *J. Org. Chem., 31* (1966) 396.