Journal of Organometallic Chemistry, 390 (1990) C73–C76
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20791PC

Preliminary communication

Synthesis of tris(trifluoromethyl)gallium and its adducts

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(Received August 14th, 1989)

Abstract

Tris(trifluoromethyl)gallium and its trimethylphosphine and trimethylarsine complexes have been synthesized using the Morrison reagent. Several new materials of potential importance to the microelectronic industry have been produced.

There is currently great interest in gallium arsenide chemistry as a consequence of strong economic incentives in the microelectronics industry [1]. Fueled by new funding made available by many U.S. government agencies, organometallic chemistry as a source of electronic materials precursors stands to become the U.S. organometallic chemical activity of the nineties, comparable in popularity to carbon–hydrogen bond activation in the seventies [2]. Currently gallium arsenide thin film chemistry is best carried out by the OMCVD (organometallic chemical vapor deposition) method for larger scale processes and typically involves the reaction of trimethylgallium with AsH_3 or PH_3 at elevated temperatures (600–700 °C) [3*]:

$$Me_3Ga + AsH_3 \rightarrow GaAs + 3CH_4\uparrow$$

There has been a long standing interest in the synthesis of trifluoromethyl-organometallic compounds in our group and perhaps more such compounds have been prepared at MIT and the University of Texas than in all other laboratories combined [4–8]. Many methods have been employed [4,9,10]. Although trimethylaluminum, -gallium, -indium and -thallium [11] derivatives have been known for years, the trifluoromethyl-substituted Group III metals are now unknown.

We report the synthesis of tris(trifluoromethyl)gallium and its trimethylarsine and trimethylphosphine adducts. To accomplish this synthesis we have used the bis(trifluoromethyl)cadmium (glyme) [7,12] pioneered and developed by John Morrison and co-workers. At present the Morrison reagent is the most versatile and effective trifluoromethyl transfer reagent in organometallic chemistry. It is more

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[*] Reference number with asterisk indicates a note in the list of references.

efficient than $Hg(CF_3)_2$ which was first used as a transfer reagent by Morrison in our laboratory [8,10].

For this specific synthesis, the most generally applicable synthetic method for trifluoromethyl organometallic compounds [6,13], the condensation reaction of metal atoms with trifluoromethyl radicals:

$$Ga + 3{}^{\cdot}CF_3 \rightarrow Ga(CF_3)_3$$

fails to produce $Ga(CF_3)_3$ but gives other gallium fluorocarbon higher polymers [14]. This rare problem is twofold: gallium metal does not vaporize primarily in its monomeric form and gallium vapor is easy to excite electronically when it enters a trifluoromethyl radical plasma region (an uncommon problem) leading to multiple reaction paths.

Bis(trifluoromethyl)cadmium · glyme can be easily prepared by the reaction of $CdMe_2$ with $Hg(CF_3)_2$ in glyme [12]. ($Hg(CF_3)_2$ was prepared by the decarboxylation reaction of $Hg(CO_2CF_3)_2$ in the presence of K_2CO_3 at 190 °C under vacuum.) Tris(trifluoromethyl)gallium is prepared by the addition of a slight excess of $Cd(CF_3)_2$ · glyme in CH_2Cl_2 to a stirred CH_2Cl_2 solution of $GaBr_3$:

$$3Cd(CF_3)_2 \cdot \text{glyme} + 2GaBr_3 \xrightarrow[25\,^{\circ}C]{CH_2Cl_2} 2Ga(CF_3)_3 + 3CdBr_2 + \text{glyme}$$

$$Ga(CF_3)_3 \xrightarrow{B:} Ga(CF_3)_3 \cdot B$$

B: = trimethylphosphine and trimethylarsine

A dropwise addition of 2.0 g (5.9 mmol) of $Cd(CF_3)_2$ · glyme in 10 ml of CH_2Cl_2 to 1.15 g (3.7 mmol) of $GaBr_3$ in 10 ml of CH_2Cl_2 led to immediate precipitation of $CdBr_2$. The solution was stirred for a few minutes before filtering off the insolubles. Recrystallization from hexane gave 0.32 g (1.2 mmol) of $Ga(CF_3)_3$ as a tan solid (31% yield). ^{19}F NMR gave a singlet in the trifluoromethyl substituted metal region (−10 to +80 ppm) (see Table 1). A qualitative base hydrolysis of $Ga(CF_3)_3$ gave CF_3H which was identified by the infrared spectrum. The mass spectrum of $Ga(CF_3)_3$ was taken using field desorption mass spectroscopy and contained molecular ion peaks at 276 and 277 and $M^+ - F$ peaks at 257 and 258. Analysis. Found: F, 61.87. $Ga(CF_3)_3$ calcd.: F, 61.78%. The compound decomposed at 350 °C without melting.

Tris(trifluoromethyl)gallium (trimethylphosphine) can be formed quantitatively by the addition of a slight excess of PMe_3 to a solution of $Ga(CF_3)_3$ dissolved in methylene chloride. The complexed compound was recrystallized from hexane. The ^{19}F and ^{1}H NMR data are in Table 1. A high resolution mass spectrum confirmed

Table 1

^{19}F NMR and ^{1}H NMR data for CF_3 gallium compounds [a]

Compound	^{19}F NMR	^{1}H NMR	J(P–H)
$Ga(CF_3)_3$	52.4	–	–
$Ga(CF_3)_3 \cdot PMe_3$	51.7	1.5d	8
$Ga(CF_3)_3 \cdot AsMe_3$	51.4	1.6	–

[a] Spectra were recorded for dilute solutions in CD_2Cl_2 at room temperature with external $CFCl_3$ and $SiMe_4$ as standards for ^{19}F and ^{1}H NMR, respectively. Shifts are in ppm and coupling constant in Hz.

the $M^+ - F$ peak, 33 m/e of the gallium 69 isotope with a 2 ppm error. (HRMS: 332.95786 found, 332.95714 calculated.) Analysis Found: F, 48.57. $Ga(CF_3)_3PMe_3$ calcd.: F, 48.48%. Crystals suitable for X-ray crystallography have been grown in THF at 0 °C. A structure determination for $Ga(CF_3)_3PMe_3$ is underway.

Similarly, $Ga(CF_3)_3$ can be complexes with $AsMe_3$ to form $Ga(CF_3)_3AsMe_3$. This compound can also be recrystallized from hexane. $Ga(CF_3)_3AsMe_3$ decomposes at 225 °C. Analysis Found: F, 43.04. $Ga(CF_3)_3AsMe_3$ calcd.: F, 43.11%.

The $(CF_3)_3GaAsMe_3$ adduct appears to be a very good single source precursor for the preparation of Group III–Group IV semiconductor materials such as gallium arsenide under mild conditions [15]. The oligomeric nature of gallium compounds of this class may be unique and crystallographic studies of the adducts are underway. Collaborations in the gallium arsenide film area are also underway.

Acknowledgement. We are grateful for support of this work by the Air Force Office of Scientific Research (AFOSR-88-0084) and the Robert A. Welch Foundation (F-700).

References

1 (a) Chemical and Engineering News, (1986, July 7), 34–48; (b) High Technology, (1986, July), 26–33; (c) National Photovoltaics Program Five Year Research Plan, 1984–1988, (May 1983), 11; (d) A.L. Fahrenbuch, R.H. Bube, Fundamentals of Solar Cells, Academic Press, New York, 1983, p. 335–346; (e) R.W. Birkmire, R.B. Hall, J.E. Phillips, 17th Conf. Rec. IEEE Photovoltaic Spec. 1984, p. 882–886; (f) R.K. Ahrenkiel, L.L. Kazmerski, R.J. Matson, C. Osterwald, T.P. Massopust, R.A. Michelsen, W.S. Chen, Appl. Phys. Lett., 43 (1983) 658; (g) J.A. Thornton, D.G. Cornog, R.B. Hall, S.P. Shea, J.D. Meakin, 17th Conf. Rec. IEEE Photovoltaic Spec., 1984, p. 781–785; (h) Chem. Eng. Prog., (1985, May, 30).

2 Pimentel Report, Opportunities in Chemistry, National Academy Press, Washington, 1985.

3 H.M. Manasevit, Appl. Phys. Lett., 12 (1968) 156. See also: T. Nakanisi, J. Cryst. Growth, 68 (1984) 282 and ref. therein. Other recent examples of CVD processes include SiO_2 on ZrO_2 and TiO_2: T. Jin, T. Okuhara, J.M. White, J. Chem. Soc., Chem. Commun., (1987) 1248. TiC on Pyrex: G.S. Girolami, J.A. Jensen, D.M. Pollina, W.S. Williams, A.E. Kaloyeros, C.M. Allocca, J. Am. CHem. Soc., 109 (1987) 1579. MB_2 (M = Ti, Zr, Hf) on Pyrex: J.A. Jensen, J.E. Gozum, D.M. Pollina, G.S. Girolami, J. Am. Chem. Soc., 110 (1988) 1643. $FeCo_x$ and $FeCo_xO_y$ on glass: C.L. Czekaj, G.L. Geoffroy, Inorg. Chem., 27 (1988) 8.

4 (a) R.A. Jacob, R.J. Lagow, J. Chem. Soc., Chem. Commun., 4 (1973) 104; (b) H. Burger, R. Eujen, R.J. Lagow, Spectrochimica Acta, A 31 (1975) 777; (c) E.K.S. Liu, R.J. Lagow, J. Am. Chem. Soc., 98 (1976) 8270; (d) J.A. Morrison, R.J. Lagow, Inorg. Chem., 16 (1977) 1823; (e) E.K.S. Liu, R.J. Lagow, J. Organomet. Chem., 145 (1978) 167; (f) D.W. Firsich, R.J. Lagow, J. Chem. Soc., Chem. Commun., 23 (1981) 1283.

5 (a) L.L. Gerchman, R.A. Jacob, J.A. Morrison, R.J. Lagow, J. Am. Chem. Soc., 97 (1975) 518; (b) L.J. Turbini, R.E. Aikman, R.J. Lagow, ibid., 101 (1979) 5833; (c) M.A. Guerra, T.R. Bierschenk, R.J. Lagow, J. Chem. Soc., Chem. Commun., (1985) 1550; (d) T.J. Juhlke, J.I. Glanz, R.J. Lagow, Inorg. Chem., 28 (1989) 980; (e) M.A. Guerra, R.J. Lagow, J. Chem. Soc., Chem. Commun., in press.

6 (a) T.R. Bierschenk, T.J. Juhlke, R.J. Lagow, J. Am. Chem. Soc., 103 (1981) 7340; (b) T.R. Bierschenk, W.I. Bailey Jr., T.J. Juhlke, R.J. Lagow, J. Organomet. Chem., 277 (1984) 1; (c) M.A. Guerra, T.R. Bierschenk, R.J. Lagow, ibid., 307 (1986) C58; (d) M.A. Guerra, T.R. Bierschenk, R.J. Lagow, Revue de Chimie Minerale, 23 (1986) 701; (e) T.R. Bierschenk, M.A. Guerra, T.J. Juhlke, S.B. Larson, R.J. Lagow, J. Am. Chem. Soc., 109 (1987) 4855.

7 M.A. Guerra, T.R. Bierschenk, R.J. Lagow, J. Am. Chem. Soc., 108 (1986) 4103.

8 J.A. Morrison, R.J. Lagow, Advances in Inorganic and Radiochemistry, 23 (1979) 199.

9 (a) R. Eujen, R.J. Lagow, Inorg. Chem., 14 (1975) 3128; (b) R. Eujen, L.L. Gerchman, J.A. Morrison, R.J. Lagow, J. Am. Chem. Soc., 100 (1978) 1722; (c) E.K.S. Liu, R.J. Lagow, Inorg. Chem., 17 (1978)

618; (d) M.A. Guerra, R.L. Armstrong, W.I. Bailey Jr., R.J. Lagow, J. Organomet. Chem., 254 (1983) 53; (e) H.H. Murray, J.P. Fackler Jr., L.C. Porter, D.A. Briggs, M.A. Guerra, R.J. Lagow, Inorg. Chem., 26 (1987) 357.

10 J.A. Morrison, L.L. Gerchman, R. Eujen, R.J. Lagow, J. Fluorine Chem., 10 (1977) 333.

11 G. Wilkinson, F.G.A. Stone, E.W. Abel, Comprehensive Organometallic Chemistry, Pergamon Press, New York, 1982.

12 (a) L.J. Krause, J.A. Morrison, J. Chem. Soc., Chem. Commun., (1980) 671; (b) L.J. Krause, J.A. Morrison, J. Am. Chem. Soc., 103 (1981) 2995; (c) J.A. Morrison, Adv. Inorg. Chem. Radiochem., 27 (1983) 293; (d) D.J. Burton, D.M. Wiemers, J. Am. Chem. Soc., 107 (1985) 5014; (e) D.J. Burton, D.M. Wiemers, ibid., 108 (1986) 832.

13 (a) T.J. Juhlke, R. Braun, T.R. Bierschenk, R.J. Lagow, J. Am. Chem. Soc., 101 (1979) 3229; (b) T.R. Bierschenk, R.J. Lagow, Inorg. Chem., 22 (1983) 359.

14 T.R. Bierschenk, Ph.D. Thesis, The University of Texas at Austin, 1982.

15 M.A. Guerra, S.K. Mehrotra, D.W. Dyer, R.J. Lagow and J.G. Ekerdt, to be published.