Methylgallium and methylindium: the first sighting of the simplest organic derivatives of Ga(I) and In(I)

Hans-Jörg Himmel,*[a] Anthony J. Downs,[a] Tim M. Greene[a] and Lester Andrews[b]

[a] *Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, UK OX1 3QR.*
E-mail: tony.downs@chem.ox.ac.uk
[b] *Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901, USA*

Received (in Basel, Switzerland) 6th September 1999, Accepted 6th October 1999

Gallium or indium atoms are shown to react with methane in solid Ar matrices upon UV photolysis (λ = 200–400 nm) to give initially the methylmetal hydride which undergoes photodissociation on broad-band irradiation (λ = 200–800 nm) to yield the methylmetal(I) compound, CH_3M (M = Ga or In); the products are characterised by their IR spectra afforced by the results of DFT calculations.

Volatile organo or hydrido derivatives of the group 13 metals excite attention particularly by virtue of their use or potential as precursors to the metal or a compound semiconductor.[1,2] Yet the number of such compounds, and especially those with the requisite properties of volatility, thermal stability, *etc.* decreases sharply when aluminium gives way to gallium, and again when gallium gives way to indium.[2,3] The only monomethyl compound of the group 13 metals to be detected previously in the laboratory is CH_3Al, which has been identified in the gas phase by its pure rotational spectrum,[4] by neutralization–reionization mass spectrometry (NRMS),[5] and also in a cooled jet by high-resolution resonance-enhanced multiphoton ionization (REMPI) spectroscopy.[6] Otherwise we are largely dependent on quantum chemical methods[7–10] for whatever knowledge of CH_3Al and CH_3Ga we possess. The incentive for characterising these molecules comes partly from their potential intermediacy in chemical vapour deposition processes starting from trivalent methylmetal compounds[1,2] and partly from the desire to gain a better understanding of the bonding in organometallic compounds of the univalent group 13 metals.

Irradiation of a CH_4-doped Ar matrix containing thermally generated gallium atoms with UV light with λ = 200–400 nm over a period of 10 min resulted in the appearance of new IR absorptions at 1719.7, 752.9, 528.7 and 475.5 cm^{-1}, apparently belonging to a single product **1a** [Fig. 1(b)]. The most intense and distinctive features were those at 1719.7 and 752.9 cm^{-1}. Similar results have been reported earlier,[11,12] the new bands being attributed to the divalent gallium species CH_3GaH formed by insertion of a Ga atom into a C–H bond of methane. Continued irradiation under these conditions produced little further change in the spectrum. By contrast, after photolysis for a further 10 min, with broad-band UV–VIS light (λ = 200–800 nm), the matrix exhibited the IR spectrum depicted in Fig. 1(c). Hence it was apparent that the bands due to **1a** had been totally extinguished, to be replaced by a new family of bands having a common origin in a second product **2a**. These occurred at 2986.9, 1403.9, 1147.9 and 476.2 cm^{-1}, the feature at lowest frequency being the most intense. Extending the period of photolysis gave little further change in the spectrum. The reaction was also followed by monitoring the UV–VIS spectrum of the matrix. Our results are in line with those of Lafleur and Parnis[11] and show that the formation of **1a** occurs at the expense of Ga atoms. The experiments were repeated using either CD_4 or $^{13}CH_4$ as the reagent; the corresponding frequencies for the normal and isotopically enriched versions of **1a** and **2a** are given in Table 1. Experiments carried out for various metal and methane concentrations show that strong signals of **2a** are obtained for conditions that have favoured the generation of **1a** (the greatest yield was achieved using a furnace temperature of 950 ºC and an argon matrix containing 2% CH_4). The obvious inference to be drawn from the IR spectra is that **2a** is the simple methylgallium(I) molecule, CH_3Ga.[13] Previous experiments with GaH_2 and InH_2 have shown that under similar photolysis conditions, cleavage of a Ga–H or In–H bond leads to the formation of the monohydrides, GaH and InH, respectively.[14] DFT calculations[15,16] lead to an

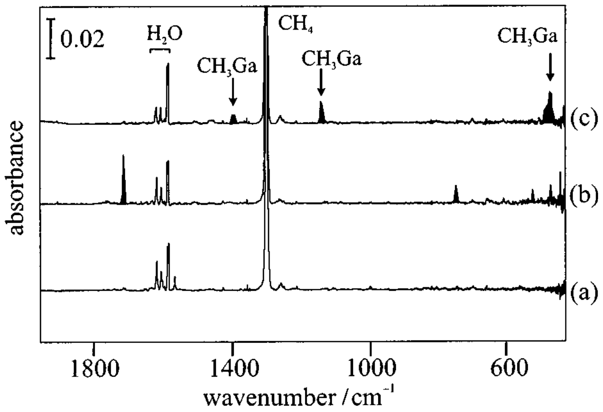

Fig. 1 IR spectra of an Ar matrix containing Ga atoms and CH_4: (a) after deposition; (b) after photolysis with UV light (λ = 200–400 nm) and (c) after broad-band UV-VIS photolysis (λ = 200–800 nm).

Table 1 Observed and calculated frequencies for CH_3Ga

$^{12}CH_3Ga$		$^{13}CH_3Ga$		CD_3Ga			Description of vibrational mode
Obs.	Calc.[a]	Obs.	Calc.[a]	Obs.	Calc.[a]	Assignment	
2986.9	2978.3 (22)	2985.8	2977.3 (23)	2200.4	2138.4 (5)	$\nu_1(a_1)$	ν_{sym}(C–H)
1147.9	1223.2 (21)	1138.8	1215.4 (18)	902.8	948.5 (36)	$\nu_2(a_1)$	$\delta_{sym}(CH_3)$
476.2	472.0 (73)	464.7	459.8 (70)	[b]	432.3 (57)	$\nu_3(a_1)$	ν(Ga-C)
[b]	3049.5 (67)	[b]	3040.7 (67)	[b]	2254.8 (36)	$\nu_4(e)$	ν_{asym}(C–H)
1403.9	1459.6 (33)	1400.1	1457.1 (33)	1025.4	1057.5 (17)	$\nu_5(e)$	$\delta_{asym}(CH_3)$
[b]	498.7 (7)	495.7	494.1 (7)	[b]	373.1 (4)	$\nu_6(e)$	$\rho(CH_3)$

[a] Calculation for singlet $CH_3{}^{69}Ga$. Symmetry C_{3v}: C–H = 1.101 Å, Ga–C = 2.049 Å, H–C–Ga = 111.7° . Intensities (km mol^{-1}) are given in parentheses; r.m.s. deviation of observed from calculated frequencies 3.7%. [b] Too weak to be observed or hiddenby methane absorptions.

Table 2 Observed and calculated frequencies for CH_3In

$^{12}CH_3In$		$^{13}CH_3In$		CD_3In			
Obs.	Calc.[a]	Obs.	Calc.[a]	Obs.	Calc.[a]	Assignment	Description of vibrational mode
2905.2	2989.1 (53)	[b]	2986.3 (54)	[b]	2141.5 (17)	$\nu_1(a_1)$	$\nu_{sym}(C–H)$
1115.3	1220.2 (42)	1107.5	1212.3 (39)	868.1	936.6 (49)	$\nu_2(a_1)$	$\delta_{sym}(CH_3)$
422.1	425.9 (53)	407.7	413.8 (50)	[b]	392.0 (41)	$\nu_3(a_1)$	$\nu(In–C)$
2976.2	3086.5 (78)	[b]	3076.1 (80)	[b]	2279.4 (38)	$\nu_4(e)$	$\nu_{asym}(C–H)$
1424.0	1475.0 (38)	1419.6	1471.6 (38)	[b]	1071.3 (22)	$\nu_5(e)$	$\delta_{asym}(CH_3)$
[b]	533.1 (0.1)	[b]	530.6 (0.1)	[b]	397.7 (0.1)	$\nu_6(e)$	$\rho(CH_3)$

[a] Calculation for singlet $CH_3{}^{115}In$. Symmetry C_{3v}: C–H = 1.103 Å, In–C = 2.226 Å, H–C–In = 111.5°. Intensities (km mol^{-1}) are given in parentheses; r.m.s. deviation of observed from calculated frequencies 5.7%. [b] Too weak to be observed or hidden by methane absorptions.

equilibrium geometry with C_{3v} symmetry for the CH_3Ga molecule. There are therefore six distinct IR-active vibrational fundamentals spanning the representation $3a_1 + 3e$. Our experiments located IR absorptions with relative intensities, frequencies and isotopic shifts in close accord with those predicted here and elsewhere[7,8] by quantum chemical calculations for four of the fundamentals (Table 1). Of the two missing features that due to ν_4 (e) was most probably masked by the strong methane absorption, whereas that due to ν_6 (e) lacked the intensity to be detected. Quantum mechanical calculations indicate that the excited electron originates in an orbital with a high electron density along the Ga–H axis,[17] so that photodissociation of the Ga–H bond may result. Other possible explanations include the formation of methylgallium from the metal atoms and methyl radicals following decomposition of methylgallium hydride to $CH_3\cdot$ and Ga and H atoms.

Analogous experiments were carried out to follow the reaction of methane with thermally evaporated In. A similar pattern was observed. Thus, irradiation of the matrix at wavelengths between 200 and 400 nm for 10 min led to the appearance of new IR absorptions at 1545.9 and 696 cm^{-1} (Fig. 2). These showed obvious affinities to the IR bands belonging to **1a** and are most plausibly ascribed to the indium analogue **1b**. Subsequent exposure of the matrix to broad-band UV-VIS radiation (λ = 200-800 nm) for 10 min brought about the disappearance of the absorptions due to **1b** with the simultaneous growth of a new set of absorptions at 2976.2, 2905.2, 1424.0, 1115.3 and 422.1 cm^{-1}. The circumstances of the experiment, allied to the spectroscopic resemblance of this second product to **2a**, suggest that it is to be identified with the indium analogue **2b**, CH_3In. The experiments giving rise to the products **1b** and **2b** were repeated using either CD_4 or $^{13}CH_4$ as the reagent, with the results included in Table 2. DFT calculations[15,16] give an optimized geometry resembling closely that of the gallium compound and having the vibrational properties listed in Table 2. In this case our experiments identify five of the six fundamentals, the only absentee being the CH_3 rocking mode, $\rho(CH_3)$, which is anticipated in any case to be unusually weak in IR absorption. Information about the isotopomers CD_3In and $^{13}CH_3In$ is unfortunately rather sparse, partly because we were unable to secure such high concentrations and partly because of the masking effects of other absorptions. Nevertheless, the experimental results approximate closely to the properties computed by DFT methods.

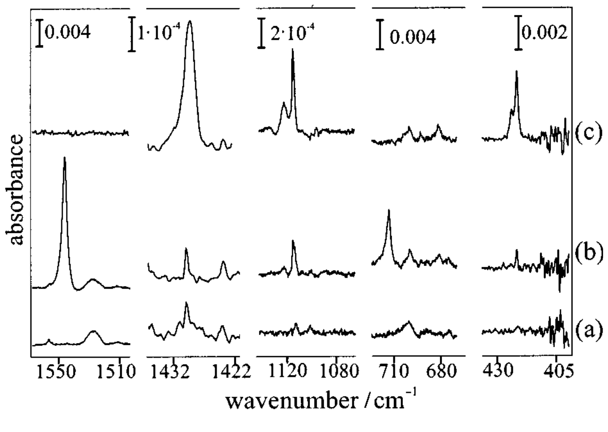

Fig. 2 IR spectra of an Ar matrix containing In atoms and CH_4: (a) after deposition; (b) after photolysis with UV light (λ = 200–400 nm); and (c) after broad-band UV–VIS photolysis (λ = 200–800 nm).

Experiments were also carried out to explore the effects of co-condensing laser-ablated indium atoms with methane and an excess of argon. In this case, IR bands due to both the products **1b** and **2b** were observed upon deposition, presumably as a result of the UV-VIS radiation emanating from the metal target. The subsequent response of the products to further photolysis was as detailed above. These experiments also support our assignments to monometallic species, as it is known[18,19] that laser ablation of solid elements generates predominantly atoms rather than aggregates.

The authors thank (i) the EPSRC for support of this research and for the award of an Advanced Fellowship to T. M. G., and (ii) the Deutsche Forschungsgemeinschaft for the award of a postdoctoral grant to H.-J. H.

Notes and references

1 *E.g.* J. R. Heath and J. J. Shiang, *Chem. Soc. Rev.*, 1998, **27**, 65.
2 *Chemistry of Aluminium, Gallium, Indium and Thallium*, ed. A. J. Downs, Blackie, Glasgow, U.K., 1993.
3 A. J. Downs, *Coord. Chem. Rev.*, 1999, **189**, 59.
4 J. S. Robinson and L. M. Ziurys, *Astrophys. J. Lett.*, 1996, **472**, L131.
5 R. Srinivas, D. Sülzle and H. Schwarz, *J. Am. Chem. Soc.*, 1990, **112**, 8334.
6 D. Clouthier, unpublished results referred to in ref. 7.
7 B. C. Hoffman, C. D. Sherrill and H. F. Schaefer III, *J. Mol. Struct. (THEOCHEM)*, 1996, **370**, 93.
8 B. S. Jursic, *J. Mol. Struct. (THEOCHEM)*, 1998, **428**, 61.
9 D. J. Fox, D. Ray, P. C. Rubesin and H. F. Schaefer III, *J. Chem. Phys.*, 1980, **73**, 3246.
10 S. Q. Jin, Y. Xie and H. F. Schaefer III, *J. Chem. Phys.*, 1991, **95**, 1834.
11 R. D. Lafleur and J. M. Parnis, *J. Phys. Chem.*, 1992, **96**, 2429.
12 Z. L. Xiao, R. H. Hauge and J. L. Margrave, *Inorg. Chem.*, 1993, **32**, 642.
13 IR absorptions attributed to methylgallium were recently observed following the high temperature decomposition of alkylgallium compounds: J. Müller, H. Sternkicker, U. Bergmann and B. Atakan, personal communication.
14 P. Pullumbi, C. Mijoule, L. Manceron and Y. Bouteiller, *Chem. Phys.*, 1994, **185**, 13.
15 DFT calculations employed GAUSSIAN 98 (B3LYP hybrid method, 6-311G* basis set for CH_3Ga and LANL2DZ for CH_3In). No scaling factor was used in the computation of vibrational frequencies.
16 GAUSSIAN 98, Revision A.3: M. J. Frisch *et al.*, Gaussian Inc., Pittsburgh PA, 1998.
17 H.-J. Himmel, T. M. Greene and A. J. Downs, unpublished work.
18 L. Andrews, D. V. Lanzisera and P. Hassanzadeh, *J. Phys. Chem. A*, 1998, **102**, 3259.
19 H. Wang, A. P. Salzberg and B. R. Weiner, *Appl. Phys. Lett.*, 1991, **59**, 935.

Communication 9/07283G