

a practical standpoint, our results demonstrate that reaction temperature is a critical variable in asymmetric reactions catalyzed by alcohol dehydrogenase<sup>9</sup> and possibly other enzymes,<sup>10</sup> and not only the optical purity but also the preferred stereochemical configuration of products may be altered by running reactions at different temperatures.

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(10) A similar reversal of stereoselectivity with increasing chain length has been observed in the reaction of pig liver esterase with dialkylidimethylmalonates, see: Bjorkling, F.; Boutelje, J.; Gatenbeck, S.; Hult, K.; Norin, T.; Szmulik, P. *Tetrahedron* **1985**, *41*, 1347. It is not clear if a similar temperature-dependent reversal would be observed in the case of pig liver esterase, since the reported reactions were performed only at 25 °C.

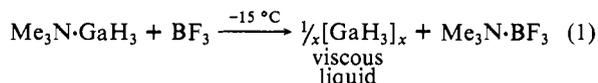
## Gallane at Last! Synthesis and Properties of Binary Gallium Hydride

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The uncoordinated binary hydride of gallium is terra incognita beyond the vapor-phase transients GaH<sup>1a</sup> and GaH<sub>3</sub><sup>1b</sup>. This has not been for want of exploration. As early as 1941 Wiberg et al. laid claim to the synthesis of the free hydride via two routes.<sup>2</sup> Neither stood the test of subsequent re-examination,<sup>3a</sup> but Greenwood and Wallbridge<sup>3b</sup> presented analytical and spectroscopic evidence for displacement reaction 1. More recent studies<sup>4,5</sup>



disclose, however, that the predominant pathway entails not displacement but *halide-hydride exchange*. Here we outline the synthesis of gallane and preliminary details of its characterization.

Of our earlier attempts to prepare gallane,<sup>5</sup> only the interaction of GaCl<sub>3</sub> with a tetrahydrogallate gave any encouragement, the solid mixture yielding at ambient temperatures small amounts of a volatile, thermally unstable product, but this could never be freed entirely from chloride. Altogether superior to GaCl<sub>3</sub> as a precursor is monochlorogallane, [H<sub>2</sub>GaCl]<sub>2</sub> **Ia**, a compound conveniently synthesized by the reaction of GaCl<sub>3</sub> with an excess of Me<sub>3</sub>SiH.<sup>6</sup> Not only is reduction already two-thirds complete,

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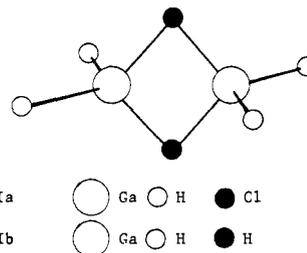
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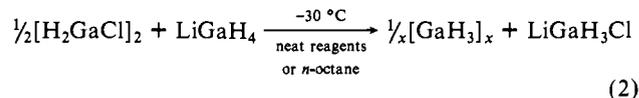
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but **Ia** is also a liquid even at quite low temperatures and therefore susceptible to more efficient mixing with the hydride ion source (MGaH<sub>4</sub>). We find that **Ia** reacts in vacuo with freshly prepared LiGaH<sub>4</sub> at -30 °C to give not only substantial quantities of elemental gallium and hydrogen but also a volatile product, shown to be gallane, typically in amounts of 4-40 mg and yields of ca. 5% based on eq 2. Operations were carried out at a pressure of



<10<sup>-4</sup> mmHg in an all-glass apparatus which had been preconditioned by heating under continuous pumping, with short distillation paths and the maintenance of all glassware to which the gallane had access at temperatures <-20 °C. Gallane condenses as a white solid which melts at ca. -50 °C and has a vapor pressure at -63 °C of ca. 1 mmHg.

(a) **Elemental analysis** confirmed that the compound contained no chlorine, only gallium and hydrogen. The reaction with an excess of anhydrous HCl at -95 °C resulted in the quantitative formation of GaCl<sub>3</sub> and H<sub>2</sub> in accordance with eq 3.



(b) **IR Spectrum.** A film of the annealed solid compound at 77 K displayed an IR spectrum resembling that of the condensate formed by the vapors derived from the reaction of an excess of NaGaH<sub>4</sub> with GaCl<sub>3</sub>,<sup>5</sup> with three main absorptions at 1778 (s), 1705 (s, br), and 550 cm<sup>-1</sup> (s, br), which shifted to 1422, 1200, and 400 cm<sup>-1</sup>, respectively, for the perdeuterated compound. Very different spectra were exhibited by the vapor (Figure 1) or by solid matrices formed by codepositing the vapor with an excess of Ar, Kr, or N<sub>2</sub> at ca. 20 K. Here the pattern and energies of the absorptions—with two distinct features near 2000 cm<sup>-1</sup> attributable to ν(Ga-H<sub>term</sub>) modes and two others at 1200-1300 cm<sup>-1</sup> attributable to ν(Ga-H<sub>bridge</sub>) modes—advocate the molecule Ga<sub>2</sub>H<sub>6</sub> with a diborane-like structure **Ib**. Of the six bands clearly discernible in the vapor spectrum three (at 1976, 1200, and 671 cm<sup>-1</sup>) had the P-R doublet structure characteristic of the parallel-type bands of just such a pseudo-linear molecule. The average P-R branch separation at 10.3 cm<sup>-1</sup> implies<sup>7</sup> then a rough value of 260 pm for the Ga...Ga distance, in excellent agreement with the corresponding distance of 261 pm in the related molecule Me<sub>2</sub>Ga(μ-H)<sub>2</sub>GaMe<sub>2</sub>, as determined by electron diffraction.<sup>8</sup> The identification of Ga<sub>2</sub>H<sub>6</sub> receives support not only from obvious parallels with the spectra of **Ia**<sup>6</sup> and Me<sub>2</sub>Ga(μ-H)<sub>2</sub>GaMe<sub>2</sub><sup>8</sup> but also from the energy shifts induced by perdeuteration of the product (see Table I). Annealing an Ar matrix containing the gallane at temperatures up to ca. 35 K caused the decay of the bands associated with Ga<sub>2</sub>H<sub>6</sub> and the appearance and growth of a spectrum resembling that of the solid gallane. Facile aggregation of Ga<sub>2</sub>H<sub>6</sub> molecules in the solid phase appears then to give an oligomer with a change in the mode of hydrogen bridging but retaining terminal Ga-H bonds (cf. α-AlH<sub>3</sub><sup>9</sup>).

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Table I. IR Spectra of Digallane in the Vapor Phase at ca. 270 K and Isolated in Solid Ar or N<sub>2</sub> Matrices at ca. 20 K

digallane- <i>h</i> <sub>6</sub>		vapor digallane- <i>d</i> <sub>6</sub> <sup>b</sup>		$\bar{\nu}_H/\bar{\nu}_D$	digallane- <i>h</i> <sub>6</sub> trapped in an Ar matrix		digallane- <i>h</i> <sub>6</sub> trapped in an N <sub>2</sub> matrix		assignment <sup>a</sup>
$\bar{\nu}/\text{cm}^{-1}$	intens <sup>a</sup>	$\bar{\nu}/\text{cm}^{-1}$	intens <sup>a</sup>		$\bar{\nu}/\text{cm}^{-1}$	intens <sup>a</sup>	$\bar{\nu}/\text{cm}^{-1}$	intens <sup>a</sup>	
1998	m	1446	m	1.3817	2015	m	2000	m	$\nu_8$ (b <sub>1u</sub> ), $\nu$ (Ga-H <sub>1</sub> )
		1434	m, sh		1996	m			
1981	R	1421	R	1.3956 <sup>d</sup>	1985	s	1985	m	$\nu_{16}$ (b <sub>3u</sub> ), $\nu$ (Ga-H <sub>1</sub> )
1970	P	1410	P		1968	m			
1278	R	914	Q	s	1283	s	1282	m	$\nu_{13}$ (b <sub>2u</sub> ), $\nu$ (Ga-H <sub>6</sub> )
1267	Q				1278	m		1253	
		1234	w	1221	s	1243	w		
		1218	sh	1213	m				
1205	R	865	R	1.3953 <sup>d</sup>	1213	m	1220	s	$\nu_{17}$ (b <sub>3u</sub> ), $\nu$ (Ga-H <sub>6</sub> )
1195	P	855	P		1208	m			
				1195	m				
1046	vw	555	R	1.3945 <sup>d</sup>	1080	vw	1075	vw	combination
		545	Q		773	m			
760	Q	488	R	vs	761	m	770	m	$\nu_{14}$ (b <sub>2u</sub> ), $\rho$ (GaH <sub>2</sub> )
700	sh				695	w		676	
676	R	479	P	vs	666	s			$\nu_{18}$ (b <sub>3u</sub> ), $\delta$ (GaH <sub>2</sub> )
666	P				659	m			
	e	439	mw		655	m	655	s	$\nu_9$ (b <sub>1u</sub> ), $\rho$ (GaH <sub>2</sub> ) <sup>f</sup>
					653	m	647	w	
					648	m			

<sup>a</sup>s strong, m medium, w weak, v very, sh shoulder, t terminal, b bridging. <sup>b</sup>The IR spectrum of this sample also included a number of weak absorptions attributable to Ga<sub>2</sub>H<sub>n</sub>D<sub>6-n</sub> (n = 1, 2, ...) or impurities containing both H and D. <sup>c</sup>Matrix splitting. <sup>d</sup>Product rule calculations give for b<sub>2u</sub> fundamentals  $P_{\text{obsd}} = \nu_{13}(\text{H})\nu_{14}(\text{H})/\nu_{13}(\text{D})\nu_{14}(\text{D}) = 1.9331$  vs  $P_{\text{calcd}} = 1.9581$  and for b<sub>3u</sub> fundamentals  $P_{\text{obsd}} = \nu_{16}(\text{H})\nu_{17}(\text{H})\nu_{18}(\text{H})/\nu_{16}(\text{D})\nu_{17}(\text{D})\nu_{18}(\text{D}) = 2.7026$  vs  $P_{\text{calcd}} = 2.7681$ . The deviations of 1.3 and 2.4%, respectively, fall in the range customarily found when observed (anharmonic) vibration frequency data are used. <sup>e</sup>Too weak to be observed. <sup>f</sup>Tentative assignment.

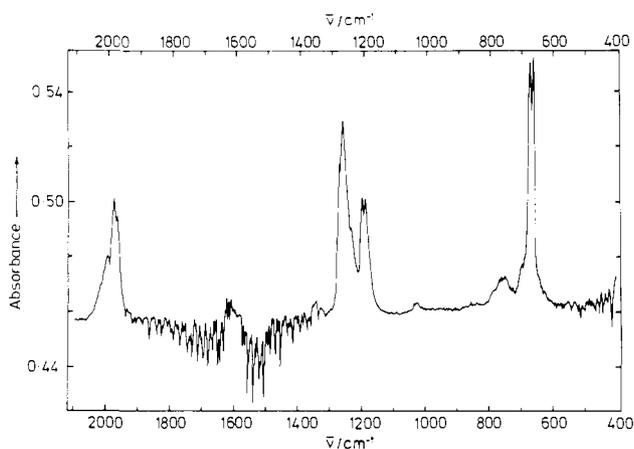


Figure 1. FT-IR spectrum of gallane vapor in a Pyrex glass cell with a pathlength of 10 cm, fitted with CsI windows and cooled to ca. 270 K; the record corresponds to the difference in absorbance between the initial, partially decomposed and final, fully decomposed sample (with appropriate scaling).

(c) <sup>1</sup>H NMR Spectrum. The <sup>1</sup>H NMR spectrum of the gallane dissolved in C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub> at -65 °C consisted of two singlets at  $\delta$  4.41 and 1.11 with relative intensities 2:1, both showing the broadness characteristic of protons directly bound to gallium atoms. This too is consistent with the structure **1b**. Coalescence to a single very broad resonance occurred when the sample was warmed to -30 °C; decomposition set in at ca. 0 °C with the appearance of gallium metal.

(d) Chemical Trapping with Trimethylamine. The gallane reacted with an excess of trimethylamine at -95 °C. At temperatures below -30 °C, there was *but a single product* identified by its IR, Raman, and <sup>1</sup>H NMR spectra as the adduct (Me<sub>3</sub>N)<sub>2</sub>GaH<sub>3</sub><sup>10</sup> this dissociated at ambient temperatures to

trimethylamine and Me<sub>3</sub>N·GaH<sub>3</sub> characterized by its vibrational spectra.<sup>10,11</sup>

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### Enantioselective Syntheses of Secondary Homoallyl Alcohols with Optically Active $\eta^3$ -Allylmolybdenum Complexes

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The enantioselective synthesis of secondary homoallylic alcohols is of interest in the context of acyclic stereoselective synthesis, with particular emphasis on their utility as biosynthetic intermediates.<sup>1</sup> The condensation of carbonyl compounds with main group organometallic allyl reagents has been a successful strategy in this respect. In particular, the use of chiral metal templates for asymmetric induction during the condensation of aldehydes with metal allyls has been developed. Chiral organometallic complexes including allylstannanes,<sup>2</sup> allylaluminum,<sup>3</sup> and allylboranes<sup>4-6</sup> react with aldehydes generating nonracemic homoallyl

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