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[10] Spectral data for **3**: $^1$H NMR (500 MHz, $CD_2Cl_2$): $\delta = 0.64$, 0.99, 1.02, 1.15 (4 d, $J = 6$ Hz; $2 \times Me_2$CH), 2.26, 2.37 (2 br. s; 2 *Me*-Ar), 2.53 (br.s; $3 \times$ *Me*-Ar), 2.62 (br. s; *Me*-Ar), 4.09–4.17 (m, $2 \times CH_2$; C*H*Me$_2$), 4.64 (septet, $J = 6$ Hz; C*H*Me$_2$), 6.91 (d, $J = 8$ Hz; CH), 6.99 (br. s; CH), 7.20–7.26 (m, 6H), 7.31 (dd, $J = 6.5$, 6.5 Hz; CH), 7.35 (d, $J = 8$ Hz; CH), 7.38 (d, $J = 9$ Hz; CH), 7.59 (s; CH), 7.82 (d, $J = 8$ Hz; CH), 7.96 (d, $J = 9$ Hz; CH), 8.02 (d, $J = 8$ Hz; CH), 16.77 (s; CH=Ru); $^{13}$C NMR (125 MHz, $CD_2Cl_2$): $\delta = 17.8$, 19.9, 20.3 ($3 \times CH_3$), 20.6 ($4 \times CH_3$), 21.0, 21.4, 21.7 ($3 \times CH_3$), 50.6, 51.6 ($2 \times CH_2$), 69.6, 78.0, 113.4 ($3 \times$ CH), 117.7, 117.8 ($2 \times$ C), 120.6, 123.3, 125.1, 125.3, 126.2, 126.3, 126.7, 127.4 ($11 \times$ CH), 127.9 (C), 128.6, 128.7, 129.3, 129.9 ($4 \times$ CH), 130.2, 133.6, 133.7, 134.0, 137.9, 138.5, 139.6, 147.3, 147.8, 152.7, 210.2 ($14 \times$ C), 297.1 (CH); HRMS *m*/*z* calcd for $C_{48}H_{52}O_2N_2Cl_2{}^{102}Ru$ [$M^+$]: 860.2443, found: 860.2451; elemental analysis calcd (%) for $C_{48}H_{52}O_2N_2Cl_2Ru$: C 66.97, H 6.09, N 3.25; found: C 66.65, H 6.11, N 3.48.

[11] $^1$H NMR data for the new compounds **21** and (*E*)-**26**; **21**: $^1$H NMR (500 MHz, $CDCl_3$): $\delta = 1.74$ (tt, $J = 6$, 7 Hz, 2H), 2.22 (dt, $J = 6$, 7 Hz, 2H), 2.29 (dt, $J = 4$, 7 Hz, 2H), 2.40 (s, 3H), 3.08 (t, $J = 6$ Hz, 2H), 3.13–3.15 (m, 2H), 5.66–5.73 (m, 2H), 7.27 (d, $J = 8$ Hz, 2H), 7.66 (d, $J = 8$ Hz, 2H); HRMS *m*/*z* calcd for $C_{14}H_{19}O_2NS$ [$M^+$] : 265.1137, found: 265.1133; (*E*)-**26**: $^1$H NMR (500 MHz, $CDCl_3$): $\delta = 1.92$–1.97 (m, 2H), 2.20 (s, 3H), 2.38 (dt, $J = 7$, 7 Hz, 2H), 4.34 (t, $J = 6$ Hz, 2H), 6.11 (d, $J = 16$ Hz, 1H), 6.81 (dt, $J = 16$, 7 Hz, 1H), 7.42 (dd, $J = 7$, 7.5 Hz, 2H), 7.54 (t, $J = 7$ Hz, 1H), 8.01 (d, $J = 7.5$ Hz, 2H); HRMS *m*/*z* calcd for $C_7H_{11}O_2$ [$M^+$ – COPh]: 127.0759, found: 127.0753.

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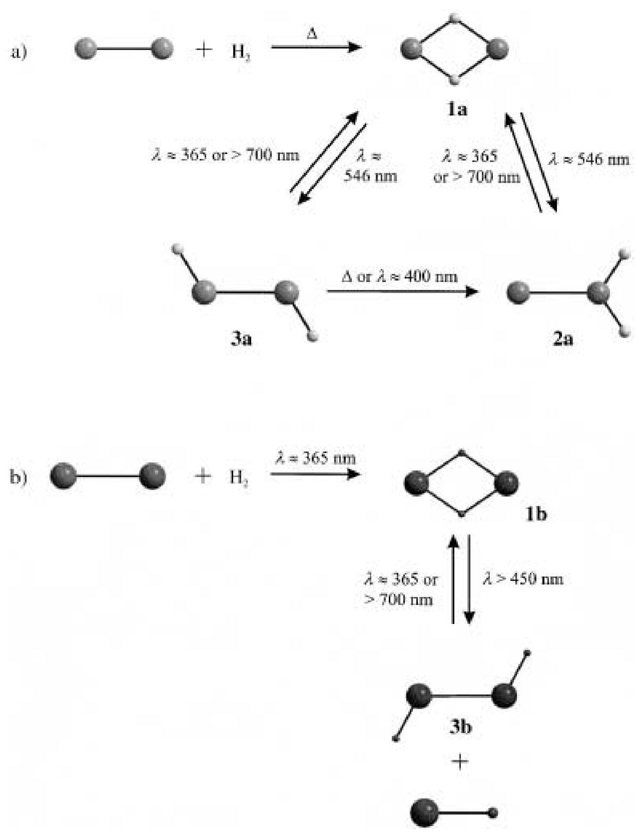
# Characterization and Photochemistry of the Gallium and Indium Subhydrides $Ga_2H_2$ and $In_2H_2$[**]

Hans-Jörg Himmel,[*] Laurent Manceron,
Anthony J. Downs, and Pluton Pullumbi

Herein we describe the cocondensation of Ga or In vapor with $H_2$ in an excess of Ar at 10–12 K, and the subsequent irradiation of the resulting matrix with light of different wavelengths. We show that the reaction of $Ga_2$ or $In_2$ with $H_2$ directly or indirectly gives rise to three isomers of $Ga_2H_2$ and two isomers of $In_2H_2$, namely the bis($\mu$-hydrido) species Ga($\mu$-H)$_2$Ga (**1a**) and In($\mu$-H)$_2$In (**1b**), the *trans*-bent species HGaGaH (**3a**) and HInInH (**3b**), and $GaGaH_2$ (**2a**) with two terminal Ga–H bonds (Scheme 1). All these molecules have been identified and characterized by IR spectroscopy, and by a comparison of the measured spectra with those calculated by quantum-chemical methods as well as with spectra of known gallium and indium hydrides. The findings show that the isomers can be interconverted by selective photolysis.



Scheme 1. Thermally and photolytically activated reactions taking place in argon matrices a) between $Ga_2$ and $H_2$, and b) between $In_2$ and $H_2$.

The Group 13 subhydrides are of interest not only because of the possibility of metal–metal bonding in M($\mu$-H)$_2$M species and even of multiple bonding in HMMH species (M = Ga or In), but also because of the potential role of gallium and indium hydrides as precursors or intermediates in chemical vapor deposition (CVD) processes designed to produce metallic or semiconductor materials. Although such compounds have attracted considerable attention from theorists,[1–4] experimental information is available only for linear HBBH[5] and for Al($\mu$-H)$_2$Al,[6] both identified in matrix experiments. Similar experiments with thermally evaporated gallium have suggested[7] that $Ga_2$ reacts spontaneously with $H_2$ to form **1a** which, like Al($\mu$-H)$_2$Al has the planar structure motif **A**. Of other possible $M_2H_2$ isomers (structure motifs **B**–**D**), only HAl($\mu$-H)Al (with structure motif **D**) has been identified, albeit somewhat tentatively.[6]

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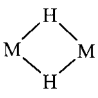
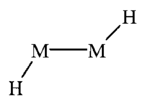
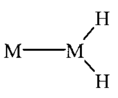


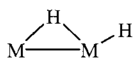
**A**



**B**



**C**



**D**

Upon deposition of gallium in a solid $H_2$-doped Ar matrix, five bands appeared in the IR spectrum of the matrix at 2200, 1176, 1002, 906.5, and 880 $cm^{-1}$, with the band at 1002 $cm^{-1}$ being an order of magnitude more intense than the other bands (Figure 1). Experiments with different concentrations of metal or $H_2$ indicated that these signals all belong to the same absorber **1a**. The relative intensities (2.3:3:1) of the triplet at 1176 $cm^{-1}$ tally almost exactly with those expected for naturally occurring $^{69}Ga$ and $^{71}Ga$ atoms with the freedom to occupy two chemically equivalent sites. Subsequent exposure of the matrix to light of the wavelength $\lambda \approx 546$ nm resulted in the extinction of the signals of **1a** and to the appearance of two sets of bands, attributable to **2a** and **3a.** Compound **2a** is marked by IR bands at 1765, 1752, and 752 $cm^{-1}$, compound **3a** by just one sharp band near 1686 $cm^{-1}$ (Figure 2, top). Compound **2a** can be converted into **3a** by heating the matrix at temperatures up to 30 K or by irradiation at $\lambda \approx 400$ nm. Photolysis at $\lambda \approx 365$ or $> 700$ nm leads then to the conversion of **2a** and **3a** back to **1a**.

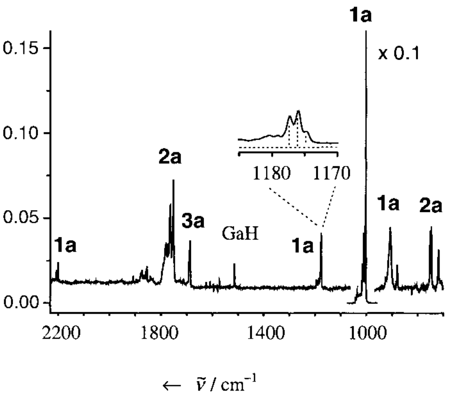


Figure 1. IR spectrum for an Ar matrix containing Ga vapor codeposited with $H_2$: ($Ga/H_2/Ar = 0.6/1/100$ deposited at 14 K for 90 min).

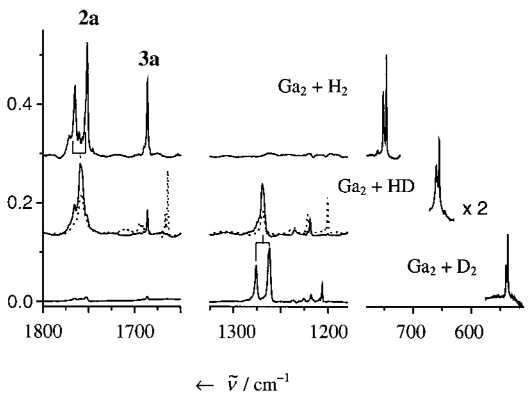


Figure 2. IR difference spectra that were obtained by subtracting the spectra recorded after irradiation at $\lambda = 600-800$ nm from those recorded after irradiation at $\lambda \approx 546$ nm for samples containing Ga vapor codeposited with 1 % $H_2$ or HD in an excess of argon. For the HD experiment, the dotted line corresponds to a spectrum recorded 1 min after excitation with green light, the solid line to a spectrum taken 120 min later, after complete evolution.

The experiments were repeated with $D_2$, HD, and 1:1 mixtures of $H_2$ and $D_2$ in place of $H_2$. In the experiments with $D_2$, only very weak IR signals attributable to the deuterium derivative of **1a** were visible immediately upon deposition. It required several hours or photolysis with IR light before the signals developed the expected level of intensity. The bands were then located near 1592, 906, 728, 653.6, and 638.4 $cm^{-1}$. The effects of photolysis were similar to those described for the reaction with $H_2$. The bands of the deuterium derivatives of **2a** and **3a** are both shifted to lower wavenumbers (**2a**: 1275.8, 1260.1, 540.3 $cm^{-1}$; **3a**: 1206.4 $cm^{-1}$; Figure 2 bottom). In the experiments with HD, signals at 2040, 1128/1112, 953, 849, and 676 $cm^{-1}$ were attributable to the **1a** analogue. The HD analogue of **2a** produced by photolysis displayed absorptions at 1758, 1270, and 665.4 $cm^{-1}$ (Figure 2, middle). The HD analogue of **3a** was also formed presumably, although at concentrations too low for it to be detected. Finally, the experiment with a 1:1 $H_2/D_2$ mixture gave spectra which were merely superpositions of those observed in the experiments with $H_2$ and $D_2$ recorded separately.

In corresponding reactions with $In_2$ instead of $Ga_2$ the formation of a reaction product was initially not observed. A reaction could be induced, however, by irradiation of the matrix at $\lambda \approx 365$ nm. This led to the appearance of five new signals at 2020.8, 1079.1, 954.8, 848, and 800.0 $cm^{-1}$, of which that at 954.8 $cm^{-1}$ was the most intense (Figure 3). On the basis of the analogies with the spectrum of **1a**, we identify the compound formed as **1b**. The intensity of signals of **1b** dropped significantly on irradiation of the matrix at $\lambda \approx 365$ nm; simultaneously two new signals appeared at 1518 and 1387.4 $cm^{-1}$. The signal at 1518 $cm^{-1}$ can be assigned to a new indium hydride species **3b**, the signal at 1387.4 $cm^{-1}$ to the known diatomic molecule InH.[8] Photolysis at $\lambda > 450$ nm led to a rapid decrease of the signal of **3b** and the reappearance of the signals of **1b**.

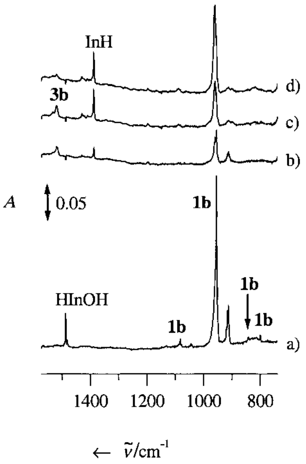


Figure 3. IR spectra recorded for an Ar matrix containing In vapor and 5 % $H_2$: a) after photolysis at $\lambda \approx 365$ nm; b) after photolysis at $\lambda > 450$ nm; c) after broad-band UV/Vis photolysis at $200 \leq \lambda \leq 800$ nm; and d) after a second cycle of photolysis at $\lambda \approx 365$ nm. HInOH, which exists as an impurity, forms by reaction with traces of $H_2O$.

Experiments with $D_2$, HD, and 1:1 mixtures of $H_2$ and $D_2$ follow the same pattern as those with gallium; the IR transitions of **1b** and **3b** are shifted to lower wavenumbers ($D_2$ experiments: **1b**: 815.1, 693.1, 611.9, 582.3 $cm^{-1}$; **3b**: 1081 $cm^{-1}$; HD experiments: **1b**: 899.6, 630.1, 605.4 $cm^{-1}$; the HD analogue to **3b** could not be detected).

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The IR spectra show that **1a**, and presumably also **1b**, contain two equivalent metal atoms. On these grounds alone, models **C** and **D** would appear to be excluded. Arguing against model **B**, moreover, is the lack of any stretching modes for terminal Ga–H or In–H bonds (1400–2050 cm$^{-1}$).[2] The most plausible interpretation of the results is that **1a** and **1b** are indeed the dihydrido-bridged molecules Ga($\mu$-H)$_2$Ga and In($\mu$-H)$_2$In with the structure **A**. For a planar molecule of this sort with $D_{2h}$ symmetry only three vibrational fundamentals are expected to be IR-active. Calculations in the optimized geometry reveal that one of these modes, corresponding to the ring-puckering mode $\nu_6(b3_u)$, will occur at a wavenumber (ca. 200 cm$^{-1}$) and with an intensity (ca. 1% that of the strongest absorption) which will make it hard to locate in practice. The intense bands at 1002 (**1a**) and 954.8 (**1b**) cm$^{-1}$ are assigned to the $\nu_4(b_{1u})$ mode and the weaker bands at 906.5 (**1a**) and 800.0 (**1b**) cm$^{-1}$ to the $\nu_4(b_{2u})$ mode. The weak bands at 880 (**1a**) and 848 (**1b**) cm$^{-1}$ can then be ascribed to the $\nu_m(b_{3g})$ mode, which is made active by the reduced symmetry ($C_{2v}$) of the $^{69}$Ga$^{71}$GaH$_2$/$^{71}$Ga$^{69}$GaH$_2$ and $^{113}$In$^{115}$InH$_2$/$^{115}$In$^{113}$InH$_2$ isotopomers, which each make up a fraction of the product. With the aid of the vibrational modes calculated for the optimized structures, the remaining bands can be attributed to combination modes each of which involves an IR-silent (a$_g$) fundamental. The net result is that all but one (b$_{3u}$) of the six fundamentals of the two molecules (2a$_g$ + b$_{3g}$ + b$_{1u}$ + b$_{2u}$ + b$_{3u}$) have been detected. The assignments are supported by isotope exchange effects ($^{69}$Ga/$^{71}$Ga and D for H).

Since the experiments with mixtures of H$_2$ and D$_2$ gave no hint of the formation of isotopomers Ga($\mu$-H)($\mu$-D)Ga or In($\mu$-H)($\mu$-D)In, which would be obtained by using HD, there can be little doubt about the concerted bimolecular nature of the reaction occurring between Ga$_2$ or In$_2$ and H$_2$. Intriguingly, though, the reaction with Ga$_2$, but not that with In$_2$, is spontaneous and shows a marked kinetic isotope effect. The reaction is much slower with D$_2$ than with H$_2$ or HD at 10–12 K, although it can be accelerated by exposure of the matrix to additional IR radiation.

Tables 1 and 2 compare the wavenumbers observed in the experiments with those calculated by using density funtional theory (DFT) methods. The contrasting reactivities of Ga$_2$ and In$_2$ pose a teasing problem to which there is no immediate solution. Possible explanations along with full details of all the results, will be reported elsewhere.[9]

Table 2. Structures and IR properties for the indium hydride species In($\mu$-H)$_2$In (**1b**) and HInInH (**3b**).[a]

| | **1b** | | **3b** | |
|---|---|---|---|---|
| symmetry | $D_{2h}$ | | $C_{2h}$ | |
| In···In | 3.4082 | | 3.0596 | |
| In–H | 2.0741 | | 1.8136 | |
| In-H-In | 110.5 | | | |
| H-In-In | | | 120.2 | |
| vibrations | obs. | calcd | obs. | calcd |
| $\nu_1$ | 1066.0[b] | 1134.2 (0, a$_g$) | [c] | 1505.5 (0, a$_g$) |
| $\nu_2$ | 124.3[b] | 140.8 (0, a$_g$) | [c] | 406.2 (0, a$_g$) |
| $\nu_3$ | 848[d] | 884.6 (0, b$_{3g}$) | [c] | 93.1 (0, a$_g$) |
| $\nu_4$ | 954.8 | 1048.5 (2268, b$_{1u}$) | [e] | 168.0 (18, a$_u$) |
| $\nu_5$ | 800.0 | 808.1 (244, b$_{2u}$) | 1518 | 1517.9 (1230, b$_u$) |
| $\nu_6$ | [f] | 332.9 (6, b$_{3u}$) | [e] | 152.2 (36, b$_u$) |

[a] Calculations at the B3PW91 level of theory; distances in Å, bond angles in °, wavenumbers in cm$^{-1}$; calculated IR intensities in km mol$^{-1}$ and symmetry assignments in parentheses. [b] Estimated value from a combination band (±5 cm$^{-1}$). [c] IR-silent. [d] See text. [e] Out of the range of detection in our experiments. [f] Too weak to be detected.

Comparison with the spectra of other gallium and indium hydrides and with the spectra simulated for different Ga$_2$H$_2$ and In$_2$H$_2$ isomers with the geometries **B**–**D**, allied with the response to deuteration, leads us to infer that **2a** is GaGaH$_2$ (**C**), and that **3a** and **3b** are HGaGaH and HInInH, respectively (**B**). The isomerization can be reversed by UV photolysis ($\lambda$ = ca. 365 nm) of HMMH (M = Ga or In) and GaGaH$_2$, or by near-IR photolysis ($\lambda > 700$ nm) of HGaGaH and GaGaH$_2$. However, there has been found as yet no trace of isomers of the type HM($\mu$-H)M (**D**). Scheme 1 summarizes the thermally or photolytically activated reactions described.

## *Experimental Section*

Gallium (Aldrich, purity 99.9999%) and indium (Aldrich, purity 99.999%) were each evaporated in either a tantalum or graphite cell or a tungsten filament that was heated resistively to about 900°C. Further details of the relevant matrix assemblies are given in references [8, 10–12]. The estimated proportions were about 0.5:0.5:100 (M/H$_2$/Ar, M/D$_2$/Ar, M/

Table 1. Structures and IR modes of the gallium hydrides Ga($\mu$-H)$_2$Ga (**1a**), GaGaH$_2$ (**2a**), and HGaGaH (**3a**).[a]

| | **1a** | | **2a** | | **3a** | |
|---|---|---|---|---|---|---|
| symmetry | $D_{2h}$ | | $C_{2v}$ | | $C_{2h}$ | |
| Ga···Ga | 3.0425 | | 2.7091 | | 2.5848 | |
| Ga–H | 1.8767 | | 1.6001 | | 1.6261 | |
| Ga-H-Ga | 108.3 | | | | | |
| H-Ga-H | | | 109.9 | | | |
| H-Ga-Ga | | | | | 121.3 | |
| vibrations | obs. | calcd | obs. | calcd | obs. | calcd |
| $\nu_1$ | 1220[b] | 1231.6 (0, a$_g$) | 1752.1[b] | 1835.8 (509, a$_1$) | [c] | 1708.9 (0, a$_g$) |
| $\nu_2$ | 175[b] | 190.1 (0, a$_g$) | 752 | 770.0 (367, a$_1$) | [c] | 502.8 (0, a$_g$) |
| $\nu_3$ | 880[d] | 920.0 (0, b$_{3g}$) | [e] | 179.3 (13, a$_1$) | [c] | 163.3 (0, a$_g$) |
| $\nu_4$ | 1002 | 1032.2 (1946, b$_{1u}$) | [f] | 359.2 (73. b$_1$) | [e] | 223.6 (24, a$_u$) |
| $\nu_5$ | 906.5 | 865.6 (213, b$_{2u}$) | 1765.1 | 1847.7 (370, b$_2$) | 1686.1 | 1727.7 (1046, b$_u$) |
| $\nu_6$ | [e] | 200.7 (18, b$_{3u}$) | [e] | 224.4 (23, b$_2$) | [e] | 186.2 (53, b$_u$) |

[a] Calculations at the B3PW91 level of theory; distances in Å, bond angles in °, wavenumbers in cm$^{-1}$; calculated IR intensities in km mol$^{-1}$ and symmetry assignments in parentheses. [b] Estimated value from a combination band (±5 cm$^{-1}$). [c] IR-silent. [d] See text. [e] Out of the range of detection in our experiments. [f] Too weak to be detected.

HD/Ar) and 0.5:1:100 ($M/H_2+D_2/Ar$). The deposition rates were about 2 mmol of matrix gas per hour.

Reagents used: $H_2$ (Air Liquide, 99.995%), $D_2$ (Isotec, 99.5%), Ar (Messer, purity 4.8). HD was prepared by reaction of $LiAlH_4$ with $D_2O$ and passed through a liquid $N_2$ trap (ca. 90% HD and 10% $H_2$).

Photolysis: high-pressure Xe/Hg arc or a medium-pressure Hg lamp (Philips LP 125, 200 or 125 W, respectively); heating effects of the matrix by IR radiation were minimized by a water filter. Light of the desired wavelengths was delivered by appropriate interference or Pyrex filters.

IR spectra of the matrix samples were recorded mostly in the reflection mode at resolutions ranging from 0.5 to 0.05 $cm^{-1}$ and with a wavenumber accuracy of $\pm 0.1$ $cm^{-1}$. FTIR spectrometers: Nicolet Magna-IR 560 (in Oxford), Bruker 113v (in Karlsruhe), and Bruker 120 (in Paris).

DFT calculations were performed with the GAUSSIAN 98 program package.[13] The results reported here are those delivered by the B3PW91 method, with a 6–311G(d) basis set for Ga and a LANL2DZ basis set with additional d-polarization functions (exponent 0.5) for In.

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# Carbonyltris(trifluoromethyl)borane, $(CF_3)_3BCO$, An Unusual Boron Carbonyl[**]

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Helge Willner,* and Friedhelm Aubke*

*Dedicated to Professor Hans Bürger*
*on the occasion of his 65th birthday*

Since the discovery of carbonylborane, $H_3B(CO)$, by Burg and Schlesinger[1] in 1937, approximately twenty further boron carbonyl derivatives have been reported and for the most part extensively characterized.[2,3] These boron carbonyls are isolable under ambient conditions, and were synthesized primarily by the addition of CO to suitable boranes and subhalogenides of boron.[2] We report here a new mononuclear boron carbonyl compound that was synthesized in an unusual manner: carbonyltris(trifluoromethyl)borane, $(CF_3)_3B(CO)$ (**1**).

The unexpected formation of **1** was observed during attempts to explore the limits of stability of salts of the new tetrakis(trifluoromethyl)borate ion $[B(CF_3)_4]^-$.[4] $K[B(CF_3)_4]$ slowly decomposes at room temperature in concentrated sulfuric acid (96%) to give a volatile product. The gas-phase IR spectrum of this product is shown in Figure 1. A preliminary identification of this material as $(CF_3)_3B(CO)$ is

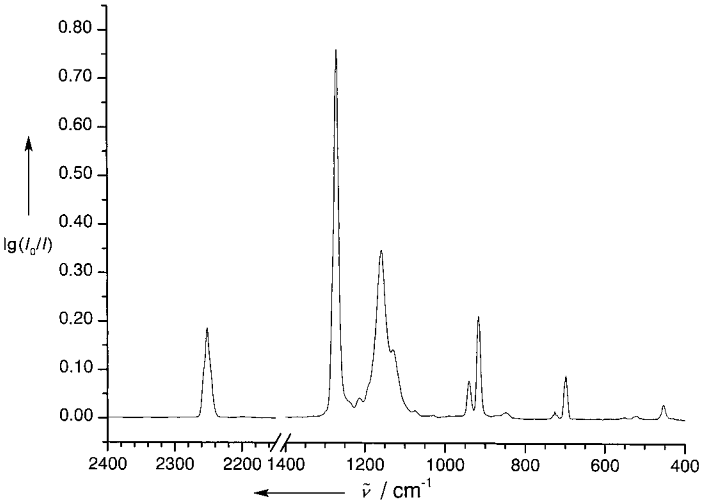

Figure 1. The gas-phase IR spectrum of **1** (0.59 mbar) at 28 °C (optical path length 19.5 cm).

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