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Organo Group 13 metal complexes of d-block elements

VII. * Stable organogalliumtetrahydroborates: novel precursors for the deposition of gallium–containing mixed metal thin films

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Abstract

Novel, mixed substituted organogallium compounds of the type $(R^1)(R^2)\overline{Ga[(CH_2)_3N}R_2]$ (R^1, $R^2 = Cl$, BH_4, alkyl, $(\eta^5\text{-}C_5H_5)(CO)_2Fe$; $R = CH_3$, C_2H_5) have been synthesized and fully characterized. These compounds are stabilized by intramolecular adduct formation at the gallium centre. The solid state structures of $[(\eta^5\text{-}C_5H_5)(CO)_2]Fe\overline{Ga[(CH_2)_3N}(CH_3)_2](R^1)$ (**3a**: $R^1 = C_2H_5$; **3d**: $R^1 = BH_4$) exhibit Fe–Ga bond lengths of 245.65(4) pm and 237.5(1) pm respectively. The Ga–B distance in **3d** amounts to 237.4(3) pm. Remarkably pure Fe/Ga thin films were grown from **3d** by low pressure OMCVD. The BH_4 group reduces both the decomposition temperature of the single source precursor and the degree of contamination by carbon of the mixed metal thin films.

1. Introduction

Organometallic chemical vapour deposition (OMCVD) and metalloorganic molecular beam epitaxy (MOMBE) show great promise as superior thin film processes since they circumvent many of the problems associated with other deposition technologies [1]. However, carbon contamination is one intrinsic problem left with organometallics as precursors for pure metals and semiconductors. Another general question is, whether single source precursors are advantageous over separate sources in adjusting the stoichiometry and phase identity of multicomponent thin films [2]. In any case, it is desirable to known more about kinetically preferred decomposition pathways which can be built into the molecular structure of the precursors, for example [3]:

$$(Me_3N)AlH_2(\eta^2\text{-}H_2BH_2)(g) \rightarrow Al(s) + 3/2H_2 + H_3BNMe_3(g) \qquad (1)$$

The key step is the migration of the amine ligand from the aluminium centre to the boron atom. Trimethylamineborane is carried away without further fragmentation and consequently Al films (free of C, N and B) were obtained. An extension of this concept to the deposition of the heavier homologues of aluminium is suggestive [3]. However, tetrahydridoborato substituted gallanes and indanes are known to decompose rapidly far below room temperature [4]. Our studies [5] on novel single source precursors for OMCVD of intermetallic materials have led us to present here our results on the synthesis, characterization and deposition properties of thermally unusually stable organogallium tetrahydridoborates and their organoiron substituted congeners.

2. Results and discussion

2.1. Synthesis and properties

The new compounds **1b–d**, **2a–b**, **3a–d** are accessible in very high yields (> 85%) by the procedures shown in Scheme 1. The compound **1e** can also be prepared by treating **1a**-Et (a derivative of **1a** with R = Et, see Table 1) with lithium tert-butylate (not shown in Scheme 1). **2a, b** are colourless, non-pyro-

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* For Part VI, see ref. 5.

** Dedicated to Prof. Dr. Dr. h.c. mult. E.O. Fischer on the occasion of his 75th birthday.

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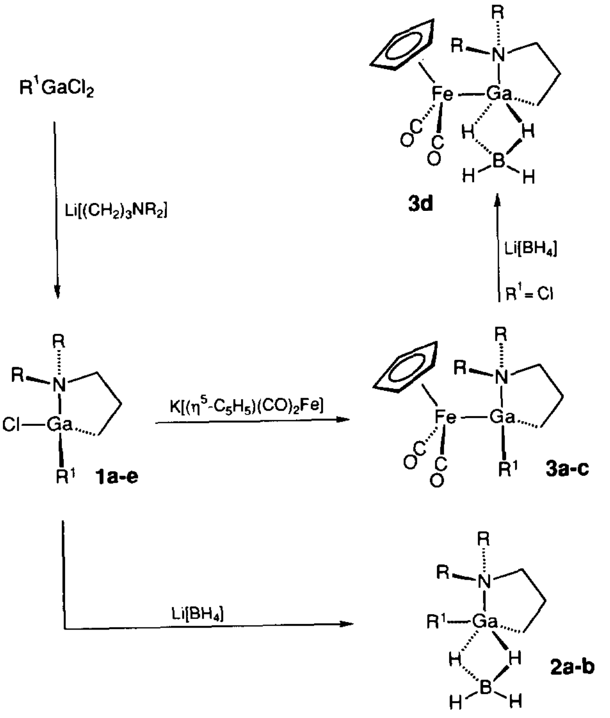

Scheme 1.

phoric and moderately air-sensitive liquids which can be purified by short path distillation *in vacuo* at 90–100°C. This thermal stability is truly remarkable, since $[(\eta^2\text{-}H_2BH_2)Ga(CH_3)_2(NMe_3)]$, the compound most closely related to **2a**, **b** is known to decompose rapidly even at −45°C into H_3BNMe_3, H_2 and gallium metal [6]. Intramolecular adduct formation proved once again to be a good route for generation of organometallic Group 13 compounds with unusual properties [7]. Sterically demanding alkyl substituents have only a little influence on the thermal stability of those systems. Traces of gallium metal however, catalyze slow decomposition of **2a**, **b** at room temperature.

TABLE 1. Numbering scheme of the compounds of Scheme 1 (Me = CH_3, Et = C_2H_5, ${}^tBu = C(CH_3)_3$, Np = $CH_2C(CH_3)_3$).

	1a	**1b**	**1c**	**1d**	**1e**	**2a**	**2b**	**3a**	**3b**	**3c**	**3d**
R^1	Cl	Et	Np	Me	^{t}Bu	Me	Np	Cl	Et	Np	–
R	Me	Me	Me	Et	Et	Et	Me	Me	Me	Me	Me

Whereas related transition metal substituted gallanes, *e.g.* those of Co [8] and Ni [9], are very sensitive towards moisture and oxygen, crystalline **3a–c** can be handled in air. The tetrahydroborato derivative **3d** is somewhat more labile and should be stored cold under nitrogen in the dark. **3a–d** sublime at 60–80°C, 10^{-3} Torr.

2.2. *Spectroscopic characterization*

The electron impact mass spectra (70 eV) of **2a**, **b** do not show the molecular peak. However, the boron-containing fragment $[(BH_4)Ga\{(CH_2)_3(NMe_2)\}^+]$, is clearly visible. Under the conditions of measurement, fragments like $[HB(CH_3)_2(NMe_2)^+]$ are observed, which are related to ligand migration processes similar to those mentioned in eqn. (1). The NMR spectra of

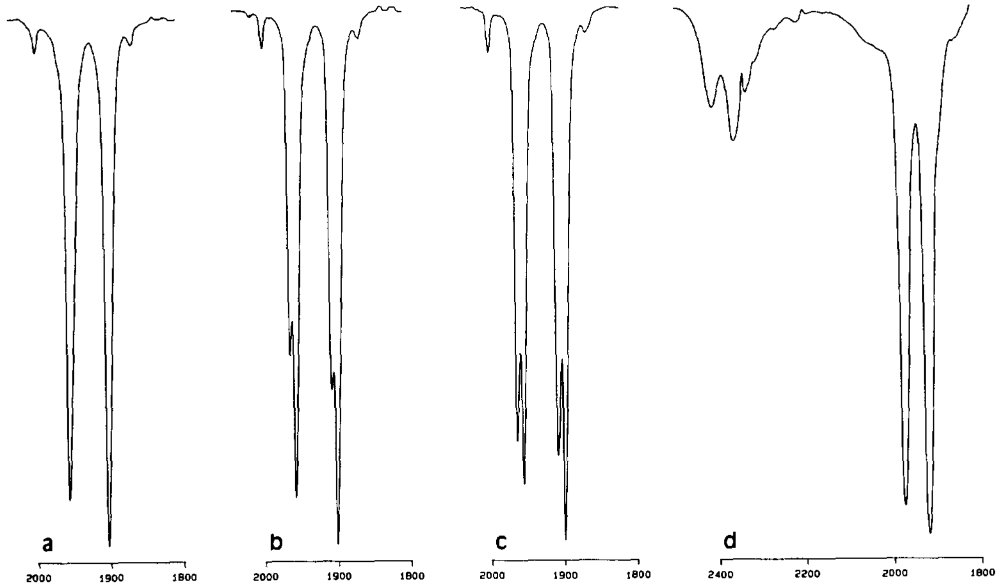

Fig. 1. Solution infrared spectra in the carbonyl region (2000–1800 cm^{-1}) obtained in CaF_2 cells (n-pentane, 25°C) for the compounds (a) **3a**, (b) **3b**, (c) **3c** and (d) **3d** (extended range: 2400–1800 cm^{-1}, including $\nu(BH_t)$ region).

the compounds **1b–e**, **2a**, **b** and **3a–d** are quite similar. The chirality of these molecules causes complex 1D-^{1}H-NMR spectra with overlapping signal groups, which were assigned by 2D-techniques [10]. Depending on the substitution pattern, the coordination sphere around the gallium centre is more or less rigid. The ^{1}H-NMR spectra of **2b** at −60°C for example, show the expected sets of multiplets for the diastereotopic protons of the metallacycle, the methyl groups at the nitrogen donor atom and the methylene group of the neopentyl substituent. The ^{11}B-NMR spectra of **2b** reveal a quintet centred at −34.8 ppm, which lies at the high field end of the range for η^2-BH$_4$-units (free BH_4^-: $-39 \cdots 45$ ppm) [11]. Likewise, the IR spectra of **2a** reveal absorptions corresponding to a η^2-BH$_4$ group at 2437, 2392 [$\nu(BH_t)$] and 2056 cm^{-1} [$\nu(BH_b)$]. These values are very similar to those known for [$(\eta^2$-$H_2BH_2)Ga\{(CH_3)_2(NMe_3)\}$] amounting to 2435, 2400 and 2080 cm^{-1}, indicating rather negatively charged BH$_4$-substituents [6]. The solution IR-spectra of the Fe–Ga species **3b**, **c** show a surprising feature. While for C_1 symmetric **3a** and **3d** only the two expected ν(CO) absorptions are observed, analytically pure **3b**, **c** exhibit four ν(CO) bands (Fig. 1). Apparently, two conformers of **3b**, **c** are resolved on the IR timescale at 25°C, which is not the case of the more rigid molecule **3a** and the more fluxional system **3d**.

2.3. *Structures of 3a and 3d*

The crystal structures of **3b** (Fig. 2a) and **3d** (Fig. 2b) have been determined. They confirm the presence of an iron–gallium bond in each compound and are consistent with the IR and NMR spectroscopic features of **3b** and **3d** in solution. The Fe–Ga bond lengths of 245.7 pm (**3b**) and 237.5 pm (**3d**) are comparable to those of [$(\eta^5$-$C_5H_5)(CO)_2$]Fe–Ga$(C_5H_4Me)_2(C_5H_5N)$, 242.7 pm [12], and of {[$(\eta^5$-$C_5H_5)(CO)_2$]Fe}$_3$Ga, 244.0 pm [13]. Intramolecular adduct formation to yield a five membered metallacycle completes the distorted tetrahedral coordination sphere around the gallium atoms in **3b** and **3d**. The Ga–N and Ga–C distances are within the range observed for related compounds [7,8]. The Ga–B distance of 237.4 pm in **3d** is considerably longer than the respective value of 215.2 pm reported for [$(\eta^2$-$H_2BH_2)Ga(CH_3)_2$] in the gas phase [6]. To our knowledge, **3d** is the first example of a tetrahydroborato gallium compound that has been structurally characterized in the solid state.

2.4. *OMCVD experiments*

Low pressure OMCVD experiments using a horizontal hot-walled tube reactor were carried out according to procedures described elsewhere [5]. The Fe–Ga systems **3a** and **3c** proved to be thermally very stable. Fe/Ga films could only be obtained above 500°C and were heavily contaminated with carbon. The ethyl derivative **3b** gave some deposition at 350°C, while most (> 90%) of the precursor compound still passed the hot zone (1 = 10 cm, Ø = 2.5 cm) unchanged and collected in the cold trap behind. The tetrahydroborato complex **3d** instead was quantitatively pyrolyzed into Fe/Ga deposits and gaseous by-products between 250 and 350°C (10^{-2} Torr). The characterization of the

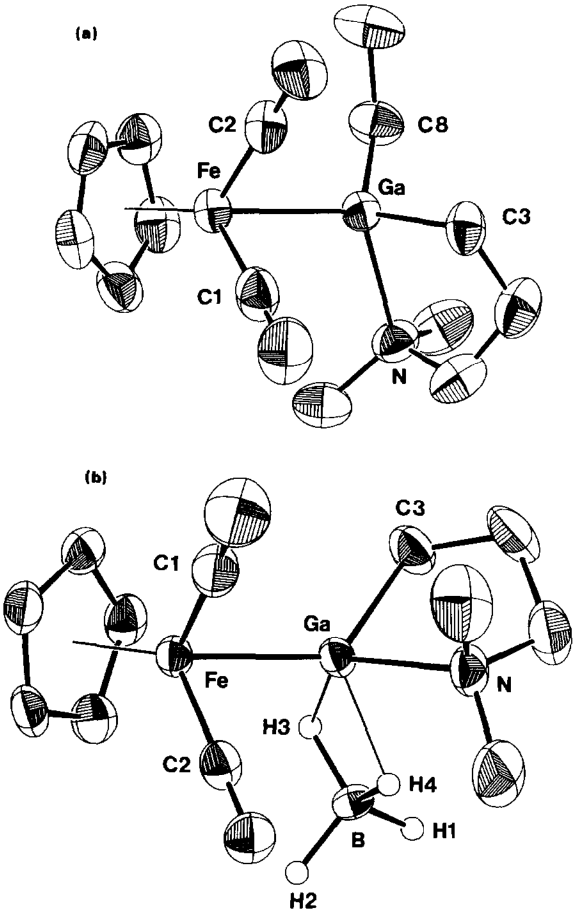

Fig. 2. (a) A view of the molecular structure of **3b** in the solid sate (ORTEP drawing, non-hydrogen atoms are shown as 50% thermal ellipsoides, hydrogen atoms are omitted for clarity). Selected bond distances (pm) and angles (degrees): Fe-Ga 245.65(4), Fe-C1 173.0(3), Fe-C2 172.8(3), Ga-C3 200.1(3), Ga-N 218.5(2), Ga-C8 200.0(3), Fe-Cp 172.6, C1-Fe-Ga 84.2(1), C2-Fe-Ga 78.4(1), C1-Fe-C2 93.3(1), Fe-Ga-C3 116.8(1), Fe-Ga-N 112.3(1), C3-Ga-N 87.1(1), C3-Ga-C8 116.9(1), N-Ga-C8 105.1(1), Fe-Ga-C8 114.4(1). (b) A view of the molecular structure of **3d** in the solid sate (ORTEP drawing, non-hydrogen atoms are shown as 50% thermal ellipsoides, hydrogen atoms are omitted for clarity, except H1 ··· H4 of the BH$_4$ substituent). Selected bond distances (pm) and angles (degrees) Fe-Ga 237.5(1), Fe-C1 174.2(4), Fe-C2 174.3(3), Ga-C3 199.1(4), Ga-N 218.5(3), Ga-B 237.4(3), Fe-Cp 171.9, C1-Fe-Ga 90.8(1), C2-Fe-Ga 82.6(1), C1-Fe-C2 96.5(2), Fe-Ga-C3 131.2(1), Fe-Ga-N 118.2(1), C3-Ga-N 87.3(1), C3-Ga-B 103.5(2), N-Ga-B 103.0(1), Fe-Ga-B 109.2(1), H1-B-H2 102.4.

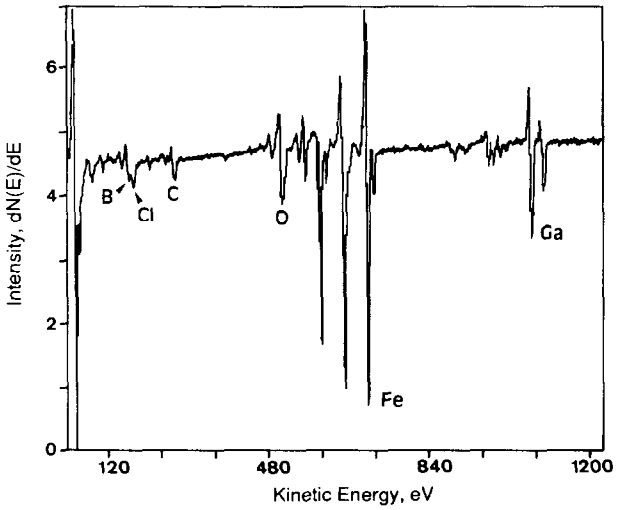

Fig. 3. AUGER spectrum (Perkin-Elmer Phi 595, 3 kV, 0.2 μA primary beam intensity) of an Fe/Ga thin film after removing surface contaminations with argon ion sputtering (2 min). Approximate composition of the thin film as calculated from the signal intensities using standard sensitivity factors [14]: Fe, 48(1); Ga, 38(1); C, 3(1), O 4(1), atom%; (N not detectable). The low contaminations of B and presumably Cl (trace impurities in the precursor compound **3d**) are difficult to quantisize due to their overlapping KLL bands.

obtained mixed metal thin films is still in progress. A typical AUGER spectrum of a roughly 4000 Å thick Fe/Ga film grown at 350°C (10^{-2} Torr) on a quartz slide is given in Fig. 3. Alkylboranes, *e.g.* H_2B-$[(CH_2)_3N(CH_3)_2]$, were detected in the effluent.

3. Conclusions

Intramolecular adduct formation at the gallium centre stabilizes organogallium tetrahydroborates and their organoiron substituted congeners to render these compounds potential precursors for the deposition of gallium-containing thin films. Remarkably pure Fe/Ga films could be grown from **3d** by low pressure OMCVD. The introduction of the BH_4 substituent at the gallium centre significantly reduces both the decomposition temperature of the single source precursor and the carbon contamination of the Fe/Ga thin films. This results show that the concept depicted in eqn. (1) might indeed be extendable to even more complex deposition problems.

4. Experimental section

All manipulations were undertaken with standard Schlenk and glove box techniques under inert gas atmosphere (purified N_2) using carefully dried (< 2 ppm H_2O) oxygen-free solvents. All samples for NMR spectra were contained in vacuum sealed NMR tubes. ^{1}H and ^{13}C NMR spectra were referenced to internal solvent and corrected to TMS. ^{11}B NMR spectra were referenced to external 10% H_3BO_3/H_2O set at −18.2 ppm. The *m/z* values are reported for ^{11}B, ^{35}Cl, ^{69}Ga and ^{56}Fe, normal isotope distribution observed. For further information concerning experimental and analytical techniques see Refs. [8,9].

4.1. Syntheses

*4.1.1. Chloro[3-(dimethylamino)propyl]ethylgallium (**1b**), chloro[3-(dimethylamino)propyl]neopentylgallium (**1c**) and chloro[3-(diethylamino)propyl]metylgallium (**1d**)*

A two necked round bottom flask (250 ml) was charged with 7.2 g (42.2 mmol) freshly sublimed $EtGaCl_2$ [15], which was dissolved in 50 ml Et_2O at −78°C. A suspension of 3.9 g (42.4 mmol) $Li[(CH_2)_3NMe_2]$ [16] in 70 ml Et_2O was then slowly added with stirring. The mixture was allowed to warm to r.t. during 1 h and stirred for an additional 5 h. After filtration and vacuum distillation of the solvent at r.t., the pure product, 8.7 g (94%), was obtained by short path distillation at 82-86°C (10^{-3} Torr, dyn. vac.). **1c** and **1d** were prepared analogously. Typical yields: > 90%.

1b: colourless liquid, bp. 82°C, 10^{-3} Torr. ^{1}H NMR (399.78 MHz, d_8-toluene, 25°C): δ 0.52 (m, 5H, Ga-CH_2CH_2 and $GaCH_2CH_3$), 1.21 (t, 2H, ^3J(H, H) = 8.0 Hz, $GaCH_2CH_3$), 1.26 and 1.55 (br, 2H, $GaCH_2CH_2$), 1.65 and 2.11 (s, br, 6H, NCH_3), 1.70 and 2.15 (br, 2H, CH_2N). ^{13}C NMR (100.5 MHz, d_8-toluene, 25°C): δ 5.4 (t, $GaCH_2CH_3$), 8.5 (t, $GaCH_2CH_2$), 10.0 (q, Ga-CH_2CH_3), 22.6 (t, $GaCH_2CH_2$), 45.5 and 46.7 (q, br, NCH_3), 62.7 (t, CH_2N). IR (neat, NaCl; selected values [cm^{-1}]): ν(C–H) 3002m, 2919vs, 2865vs, 2813m; δ(C–H) 1466vs, 1436m, 1418m, 1323m, 1281m; others: 1035s, 977s, 907s, 772s, 697s, 645s. Anal. calc. for $C_7H_{17}ClGaN$ (found) C, 38.15 (37.90); H, 7.77 (7.74); N, 6.36 (6.57); Cl, 16.09 (16.05); Ga, 31.63 (31.10)%.

1c: white solid, mp. 36°C. ^{1}H NMR (399.78 MHz, d_8-toluene, 25°C): δ 0.65 and 0.95 (d, ^1J(H, H) = 13.2 Hz; 2H, $GaCH_2CMe_3$), 0.75 (br, 2H, $GaCH_2CH_2$), 1.25 and 1.55 (br, 2H, $GaCH_2CH_2$), 1.50 and 2.06 (s, 6H, NCH_3), 1.61 and 2.15 (br, 2H, CH_2N). ^{13}C NMR (100.5 MHz, d_8-toluene, 25°C): δ 11.3 (t, $GaCH_2CH_2$), 22.7 (t, $GaCH_2CH_2$), 31.2 (t, $GaCH_2CMe_3$), 33.3 (s, CH_2CMe_3), 34.0 (q, $C(CH_3)_3$), 43.9 and 46.6 (q, NCH_3), 62.4 (q, CH_2N). IR (nujol mull, NaCl; selected values, [cm^{-1}]): δ(C–H) 1464vs, 1420m, 1412m, 1381 m, 1362m; other 1036s, 1025s, 981s, 905s, 865m, 773s, 720s, 692s, 628s. Anal. calc. for $C_{10}H_{23}ClGaN$ (found): C, 45.76 (45.78); H, 8.83 (8.63); N, 5.34 (5.32); Cl, 13.51 (13.39); Ga, 26.56 (25.80)%.

1d: white solid, mp. 34°C. ^1H NMR (60 MHz, C_6D_6, 25°C) δ − 0.1 (s, 3H, $GaCH_3$), 0.70 (t, 6H, $-CH_2CH_3$) 0.50 (t, 2H, $GaCH_2$), 1.20–1.70 (m, br, 2H, $GaCH_2CH_2$), 2.03–2.56 (m, 6H, NCH_2). Anal. calc. for $C_8H_{19}NClGa$ (found): C, 40.99 (40.76); H, 8.17 (8.15); N 5.98 (5.87)%.

4.1.2. *Chloro[3-(diethylamino)propyl](tert-butyl)gallium (1e)*

Tert-butyllithium (540 mg; 8.43 mmol) dissolved in toluene (20 ml) was added dropwise to a solution of 2.16 g (8.48 mmol) **1a**-Et (derivative of **1a**: R = Et, see Table 1) in 50 ml toluene at −78°C. The reaction mixture was allowed to warm to r.t. during 1 h and was stirred for an additional 3 h. Work up according to the procedure above gave 1.92 g (82%) **1e**.

1e: colourless liquid, bp. 73–78°C, 10^{-3} Torr. ^1H NMR (399.78 MHz, d_8-toluene, 25°C) δ 0.42 and 0.80 (t, 6H, $-CH_2CH_3$) 0.44–0.63 (AA'BB', 2H, $GaCH_2$), 1.13 (s, 9H, $C(CH_3)$), 1.18–1.63 (AA'BB'CC', 2H, $GaCH_2CH_2$), 1.99–2.05 (AA'BB', 2H, CH_2CH_2N), 2.04–2.16, 2.19–2.21, 2.36–2.52 and 2.76–2.92 (ABX_3, 4H, NCH_2CH_3). ^{13}C NMR (100.5 MHz, d_8-toluene, 25°C) δ 5.5 and 10.8 (q, NCH_2CH_3), 5.7 (t, $GaCH_2$), 21.8 (t, $GaCH_2CH_2$), 23.7 (s, CMe_3), 30.3 (q, $C(CH_3)_3$), 41.6 and 46.2 (t, NCH_2CH_3), 56.4 (t, CH_2CH_2N). IR (neat): ν(CH) 2981m, 2950s, 2919s, 2872m, 2841s; δ(CH) 1469s, 1387m, 1359m; others: 1037m, 1014m, 952m, 811m, 732m, 688w. EI-MS (20°C, 70 eV): m/z (%) = $[M^+]$ 275 (n. obs.), $[M^+ - Cl]$ 240 (23), $[M^+ - C_4H_9]$ 218 (100), $[M^+ - Cl - C_4H_9]$ 183 (3), $[(C_2H_5)_2NCH_2CHCH_2]$ 113 (23), $[(C_2H_5)_2NCH_2^+]$ 86 (88), $[C_4H_9^+]$ 57 (25). Anal. calc. for $C_{11}H_{25}NClGa$ (found): C, 46.79 (46.78); H, 9.04 (9.11); N, 4.74 (5.07)%.

4.1.3. *[3-(diethylamino)propyl]methyl(η^2-tetrahydroborato)gallium (2a) and [3-(dimethylamino)propyl]neopentyl(η^2-tetrahydroborato)gallium (2b)*

To a solution of 1.42 g (6.1 mmol) **1d** in Et_2O 128 mg (6.1 mmol) of solid $Li[BH_4]$ was added at −10°C. The mixture was stirred at this temperature for a period of 12 h. The deposited LiCl was removed by filtration (230 mg; 89%). The obtained solution was then concentrated at room temperature *in vacuo*. The product was finally purified by short path distillation at 85–88°C (10^{-3} Torr, dyn. vac.). Pure **2a** was obtained as a colourless, non-pyrophoric, air-sensitive liquid (1.10 g, 85%). **2b** was prepared analogously from 2.50 g (9.5 mmol) **1c** and 210 mg (10 mmol) $Li[BH_4]$. Yield: 2.13 g (93%).

2a: ^1H NMR (60 MHz, C_6D_6, 25°C) δ −0.1 (s, 5H, $GaCH_2$ and $GaCH_3$), 0.70 (t, 6H, $-CH_2CH_3$), 1.50 (quint. br, 2H, $GaCH_2CH_2$), 1.93–2.63 (m, 6H, NCH_2). ^{13}C NMR (100.5 MHz, d_8-toluene, −50°C): δ 6.03 (q. $GaCH_3$), 7.9 and 9.6 (q, NCH_2CH_3), 8.6 (t, $GaCH_2$), 21.9 (t, $GaCH_2CH_2$). 41.4 and 46.2 (q, NCH_3), 55.6 (q, CH_2N). ^{11}B NMR (128.3 MHz, C_6D_6, 25°C): δ −35.4 (quint, $^1J(^{11}B, H)$ 82 Hz). IR (nujol mull, NaCl; selected values, [cm^{-1}]): ν(B–H) 2437s, 2392s, 2056m. Anal. calc. for $C_8H_{23}BGaN$ (found): C, 44.94 (44.78); H, 10.84 (11.05); N, 6.55 (6.35)%.

2b: colourless liquid, bp. 96°C (10^{-3} Torr). ^1H NMR (399.78 MHz, d_8-toluene, −60°C): δ 0.45 and 0.85 (d, $^1J(H, H) = 13.4$ Hz; 2H, $GaCH_2CMe_3$), 0.65 (br, 2H, $GaCH_2CH_2$), 1.22 and 1.65 (br, 2H, $GaCH_2CH_2$), 1.78 and 1.99 (s, 6H, NCH_3), 1.85 and 2.20 (br, 2H, CH_2N). ^{13}C NMR (100.5 MHz, d_8-toluene, −60°C): δ 11.4 (t, $GaCH_2CH_2$), 22.7 (t, $GaCH_2CH_2$), 31.4 (t, $GaCH_2CMe_3$), 32.3 (s, CH_2CMe_3), 33.8 (q, $C(CH_3)_3$), 44.4 and 46.8 (q, NCH_3), 62.6 (q, CH_2N). ^{11}B NMR (128.3 MHz, C_6D_6, 25°C): δ −34.8 (quint, $^1J(^{11}B, H)$ 82 Hz). IR (nujol mull, NaCl; selected values, [cm^{-1}]): ν(B–H) 2439s, 2395s, 2058m. EI-MS (25°C, 70 eV) m/z (%) = $[M^+]$ 241 (n. obs.). $[M^+ - \{CH_2CMe_3\}]$ 170 (20), $[HGa\{(CH_2)_3NMe_2\}^+]$ 156 (100), $[HB\{(CH_2)_3NMe_2\}^+]$ 98 (10). Anal. calc. for $C_{10}H_{27}BGaN$ (found): C, 49.66 (49.38); H, 11.25 (11.15); N, 5.79 (5.65)%.

4.1.4. *Chloro[η^5-cyclopentadienyl)(dicarbonyl)iron]-[3-(dimethylamino)propyl]gallium (3a), [η^5-cyclopentadienyl)(dicarbonyl)iron]ethyl[3(dimethylamino)propyl]-gallium (3b) and [η^5-cyclopentadienyl)(dicarbonyl)-iron][3-(dimethylamino)propyl]neopentylgallium (3c)*

A solution of 7.4 mmol $K[(\eta^5-C_5H_5)(CO)_2Fe]$ in 50 ml THF was prepared by reduction of 1.30 g (3.7 mmol) $[(\eta^5-C_5H_5)(CO)_2Fe]_2$ with 1.00 g (7.4 mmol) potassium graphite (C_8K) according to a procedure published elsewhere [9]. This solution was then cooled to −78°C. 1.70 g (7.5 mmol) **1a**, dissolved in 20 ml THF, was then quickly added with vigorous stirring. The stirred reaction mixture was then allowed to warm to r.t. within 1 h. After filtration and removing the solvent *in vacuo*, the off-white residue obtained was washed three times with 25 ml *n*-pentane at 0°C. The crude product was further purified by recrystallization from concentrated toluene solutions layered with *n*-heptane at 25°C to −78°C; yield: 2.4 g (88%). **3b** and **3c** were each prepared analogously from 0.80 g (2.3 mmol) $[(\eta^5-C_5H_5)(CO)_2Fe]_2$ and 0.62 g (4.5 mmol) C_8K with 1.00 g (4.5 mmol) **1b** and 1.20 g (4.5 mmol) **1c** respectively. However, due to the good solubility of **3b**, **c** in hydrocarbons the products were extracted (rather than washed) with *n*-pentane. Crystallization at −78°C from the combined, concentrated and filtered extracts gave 1.34 g (82%) **3b** and 1.56 g (86%) **3c** respectively.

3a: nearly colourless crystals, mp. 72°C, subl. 60°C 10^{-3} Torr; ^1H NMR (399.78 MHz, d_8-toluene, 25°C): δ

0.85 and 0.98 (AA'BB', 2H, GaCH$_2$), 1.47 (AA'BB'CC', 1H, GaCH$_2$C*H*$_2$), 1.68–1.80 (m, 2H; AA'BB'CC, GaCH$_2$C*H*$_2$ and AA'BB', CH$_2$N), 1.90 and 2.36 (s, 6H, NCH$_3$), 2.44 (m, 1H, AA'BB', CH$_2$N), 4.32 (s, C$_5$H$_5$). ^{13}C NMR (100.5 MHz, d_8-toluene, 25°C): δ 18.2 (t, GaCH$_2$), 22.9 (t, GaCH$_2$*C*H$_2$), 43.9 and 47.2 (q, NCH$_3$), 62.2 (s, CH$_2$N), 82.5 (d, C$_5$H$_5$; with ^{1}H-decoupling below -50°C; four out of five diastereotopic C$_{ring}$ atoms are resolved), 217.8 and 217.4 (s, FeCO). IR (*n*-pentane, cm^{-1}): ν(CO) = 1977vs, 1924vs. EI-MS (35°C, 70 eV) m/z (%) = [M$^+$] 367 (1), [M$^+$ − Cl] 332 (25). Anal. calc. for C$_{12}$H$_{17}$ClFeGaNO$_2$ (found): C, 39.14 (39.15); H, 4.70 (4.65); N 3.75 (3.80)%.

3b: slightly reddish crystals, mp. 66°C, subl. 60°C 10^{-3} Torr; ^{1}H NMR (399.78 MHz, d_8-toluene, -30°C): δ 0.59 (t, ^3J(H, H) = 8.0 Hz; 2H, GaC*H*$_2$CH$_3$), 0.74 and 0.84 (AA'BB', 2H, GaC*H*$_2$CH$_2$), 1.62 and 1.74 (AA'BB'CC', 2H, GaCH$_2$C*H*$_2$), 1.78 and 1.91 (s, 6H, NCH$_3$), 1.80 and 2.05 (AA'BB', 2 H, CH$_2$N), 4.17 (s, C$_5$H$_5$). ^{13}C NMR (100.5 MHz, d_8-toluene -30°C): δ 12.0 (q, GaCH$_2$*C*H$_3$), 13.0 (t, GaCH$_2$), 13.6 (t, GaCH$_2$), 24.5 (t, GaCH$_2$*C*H$_2$), 46.5 and 47.1 (q, NCH$_3$), 64.1 (t, CH$_2$N), 81.1 (d, C$_5$H$_5$), 219.5 and 219.8, (s, FeCO). IR (n-pentane, cm^{-1}): ν(CO) = 1968s, 1960vs, 1911s; 1904vs. EI-MS (25°C, 70 eV) m/z (%) = [M$^+$] 361 (1), [M$^+$ − {η^5-C$_5$H$_5$Fe(CO)$_2$}] 184 (100). Anal. calc. for C$_{14}$H$_{22}$FeGaNO$_2$ (found): C, 46.46 (46.54); H, 6.13 (6.22); N 3.87 (3.73)%.

3c: colourless crystals, mp. 72°C, subl. 60°C 10^{-3} Torr; ^{1}H NMR (399.78 MHz, d_8-toluene, -30°C): δ 0.82 and 0.91 (d, ^1J(H, H) = 13.4 Hz; 2H, GaC*H*$_2$CMe$_3$), 0.93 and 1.02 (AA'BB', 2H, GaC*H*$_2$CH$_2$), 1.58 and 1.81 (AA'BB'CC', 2H, GaCH$_2$C*H*$_2$), 1.74 and 1.91 (s, 6H, NCH$_3$), 1.81 and 2.30 (AA'BB', 2H, CH$_2$N), 4.17 (s, C$_5$H$_5$). ^{13}C NMR (100.5 MHz, d_8-toluene, -30°C): δ 17.7 (q, Ga*C*H$_2$CH$_2$), 24.3 (t, GaCH$_2$*C*H$_2$), 32.1 (s, *C*Me$_3$), 34.1 (q, C(*C*H$_3$)$_3$), 39.7 (t, Ga*C*H$_2$CMe$_3$), 46.7 and 48.1 (q, NCH$_3$), 63.6 (t, CH$_2$N), 81.4 (d, C$_5$H$_5$), 219.6 and 220.3 (s, FeCO). IR (n-pentane, cm^{-1}): ν(CO) = 1967s, 1956vs, 1910s, 1900vs. EI-MS (25°C, 70 eV): m/z(%) = [M$^+$] 403 (n. obs.), [M$^+$ − {CH$_2$C(CH$_3$)$_2$}] 332 (5), [M$^+$ − {CH$_2$C(CH$_3$)$_3$}] − 2 CO] 276 (2), [M$^+$ − {η^5-C$_5$H$_5$Fe(CO)$_2$}] 226 (100). Anal. calc. for C$_{17}$H$_{28}$FeGaNO$_2$ (found): C, 50.54 (50.39); H, 6.99 (6.88); N, 3.47 (3.34); Fe, 13.82 (14.66); Ga 17.26 (16.70)%.

*4.1.5. [η^5-Cyclopentadienyl)(dicarbonyl)iron][3-(dimethylamino)propyl](η^2-tetrahydroborato)gallium (**3d**)*

4.10 g (11.1 mmol) **3a** was dissolved in 50 ml Et$_2$O at 0°C. A solution of 265 mg (12.2 mmol) Li[BH$_4$] dissolved in 20 ml Et$_2$O was then added in one portion. While stirring the mixture at 0°C for 2 h, a white precipitate separated. The slightly yellow-orange coloured solution was filtered and all volatile constituents were removed *in vacuo*. The oily orange-brown residue was dissolved in a minimum amount of toluene (5 ml). This solution was filtered again and carefully layered with 20 ml n-heptane. Slow cooling from 0°C to -50°C afforded 2.82 g (73%) **3d** as well-shaped yellow-orange prisms.

3d: yellow-orange crystals, mp. 63°C, subl. 60°C 10^{-3} Torr; ^{1}H NMR (399.78 MHz, d_8-toluene, -60°C): δ 0.95 and 1.25 (AA'BB', 2H, GaC*H*$_2$CH$_2$), 1.33 and 1.57 (AA'BB'CC', 2H, GaCH$_2$C*H*$_2$), 1.65 and 1.93 (s, 6H, NCH$_3$), 1.68 and 1.95 (AA'BB', 2H, CH$_2$N and NCH$_3$), 4.15 (s, C$_5$H$_5$). ^{13}C NMR (100.5 MHz, d_8-toluene, -50°C): δ 18.0 (t, Ga*C*H$_2$CH$_2$), 23.0 (t, GaCH$_2$*C*H$_2$), 45.2 and 47.4 (q, NCH$_3$), 62.5 (t, CH$_2$N), 82.2 (d, C$_5$H$_5$; with ^{1}H decoupling: three out of five diastereotopic C$_{ring}$ atoms could be resolved), 217.2 and 216.5, (s, FeCO). ^{11}B NMR (128.3 MHz, d_8-toluene, 25°C): δ − 31.3 (quint., ^1J(^{11}B–H) = 85 Hz); IR (toluene, cm^{-1}): ν(CO) = 1975vs, 1920vs; ν(B–H$_t$) = 2419 m, 2376 m. EI-MS (25°C, 70 eV) m/z(%) = 347 [M$^+$] (n. obs.), 332 [M$^+$ − (BH$_3$)] (2), 156 [HGa(CH$_2$)$_3$N(CH$_3$)$_2^+$] (42), 58 [CH$_2$N(CH$_3$)$_2^+$] (100). Anal. calc. for C$_{12}$H$_{21}$BFeGaNO$_2$ (found): C, 41.46 (40.94); H, 6.09 (5.44); N 4.03 (3.14)%.

*4.2. Single crystal structure determination of **3b** and **3d***

X-ray structure of **3b**: $a = 785.2(3)$, $b = 1494.7(2)$, $c = 1349.2(4)$ pm, $\beta = 91.45(2)°$, $V = 1583 \cdot 10^6$ pm^3, data collection at 23°C, $\rho_{calc} = 1.519$ gcm^{-3}, $\mu = 26.1$ cm^{-1}, $F_{(000)} = 744$, $Z = 4$, monoclinic crystal system, space group $P\ 2_1/n$ (No. 14), Enraf-Nonius CAD4. $\lambda = 71.07$ pm (Mo$_{K\alpha}$, graphite monochromator), range of measurement $1.0° < \Theta < 25°$, ω-scan, scan width ($1.3 + 0.3 \tan \Theta$)° (±25% before and after each reflection to determine the background), $t_{max} = 90$ s. 3114 measured reflections (h, k, ±1), 2560 independent reflections of which 2363 had $I > 2 \cdot \sigma(I)$, structure determination with Patterson methods and difference Fourier syntheses, empirical absorption correction based on Ψ-scan data, transmission coefficients 0.789–0.997, 260 least squares parameters, all 19 heavy atoms with anisotropic thermal parameters, all 22 hydrogen atoms found and independently refined (isotropic), anomalous dispersions [17] accounted for, shift/error < 0.0001, $R = \Sigma(\| F_o| - |F_c \|)/\Sigma|F_o| = 0.0287$, $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.032$, residual electron density $+0.86$ ΔeÅ^{-3} (100 pm besides Fe)/ − 0.31 ΔeÅ^{-3}, weighting scheme of Tukey and Prince [18] with three refined parameters P(1) = 1.62, P(2) = 0.222, P(3) = 1.30.

X-ray structure of **3d**: $a = 834.7(1)$, $b = 1157.2(1)$, $c = 1614.0(1)$ pm, $\beta = 102.15(1)°$, $V = 1524 \cdot 10^6$ pm^3, data collection at -80°C, $\rho_{calc} = 1.522$ g cm^{-3}, $\mu = 97.7$ cm^{-1}, $F_{(000)} = 712$, $Z = 4$, monoclinic crystal system, space group $P2_1/n$ (No. 14), Enraf-Nonius CAD4, $\lambda = 154.18$ pm (Cu$_{K\alpha}$), range of measurement $1.0° < \Theta < 70°$, $\omega/2\Theta$-scan, scan width $(1.0 + 0.25 \tan \Theta)°$ ($\pm 25\%$), $t_{max} = 90$s, 5896 measured reflections ($\pm$h, k, $\pm$1), 2797 independent reflections of which 2343 had $I > 3.4 \cdot \sigma(I)$, structure determination with Patterson methods and difference Fourier syntheses, empirical absorption correction based on Ψ-scan data, transmission coefficients 0.434–1.0, 207 least squares parameters, all 18 heavy atoms with anisotropic thermal parameters. Hydrogen atoms: from a total of 21 hydrogen atoms 11 hydrogen atoms bonded to carbon atoms were found by difference Fourier techniques and independently refined (isotropic), 6 hydrogen atoms bonded to carbon atoms were placed in ideal geometry and included in structure factors calculations but not refined. H1 and H2 of the BH_4 group were found, H3 and H4 were placed in ideal geometry and the whole BH_4 unit was then included in the structure factor calculations as riding group. Anomalous dispersions [17] accounted for, shift/error < 0.0001, $R = \Sigma(\|F_o| - |F_c\|)/\Sigma|F_o| = 0.0397$, $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.0449$, residual electron density $+0.76$ ΔeÅ^{-3} (129 pm beside C6)/$-$0.40 ΔeÅ^{-3}, weighting scheme of Tukey and Prince [18] with three refined parameters P(1) = 3.85, P(2) = 0.0352, P(3) = 3.17.

All calculations were performed on a DECstation 5000/25 using the programs CRYSTALS [19] and PLATON [20]. Further information on the crystal structure determinations can be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich technische Information mbH, W-76344 Eggenstein-Leopoldshafen, under the depository number CSD-57617, the names of the authors and the journal citation.

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