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The first volatile Di(organogallio) transition metal Carbonylates: *cis*-$(CO)_4Fe\{Ga[(CH_2)_3NMe_2](R)\}_2$ ($R \equiv {}^tBu$ or C_6H_5), Precursors for Gallium Rich Thin Fe–Ga Alloy Films ☆

Roland A. Fischer *, Markus. M. Schulte, Thomas Priermeier

Anorganisch-chemisches Institut der Technischen Universität München, Lichtenbergstraße 4, D-85747 Garching, Germany

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Abstract

cis-$(CO)_4Fe\{Ga[(CH_2)_3NMe_2](R)\}_2$ ($R \equiv {}^tBu$ (**1a**) or C_6H_5 (**1b**)), the first examples of previously unknown transition metal gallium complexes of the type $[L(CO)_nM][GaR_2(Do)]_a$ ($a > 1$), exhibiting a gallium-to-transition-metal ratio $[Ga]/[M] > 1$, have been synthesized in high yields by the reaction of $[(CO)_4Fe]K_2$ with the mixed alkylated and intramolecularly base stabilized organo gallium chlorides $ClGa[(CH_2)_3NMe_2](R)$. The new compounds were characterized by elemental analysis, IR, NMR and mass spectrometry. Compound **1a** sublimes without decomposition and served as a gallium-rich single-source precursor to deposit remarkably pure gallium-rich Fe_1Ga_{2-x} ($x \leqslant 0.1$) thin films by low pressure metal–organic chemical vapor deposition at very low temperatures (about 200°C; 0.1 Pa).

Keywords: Gallium; MOCVD; Thin alloy films; Iron; Metal carbonylanions

1. Introduction

Transition metal gallides, aluminides and indides are of interest as epitaxial and thermodynamically stable metal III–V semiconductor interfaces [2]. We have shown previously that the organometallic mixed-metal complexes $L(CO)_nM{-}ER_2(Do)$ (type I; $R \equiv$ alkyl, $L \equiv CO$, PR_3, or Cp; $Do \equiv O$, N; Lewis base donor) can serve as single-source precursors for the deposition of the respective phase pure intermetallic thin films ME_{1-x} ($0 \leqslant x \leqslant 0.5$), e.g. β-CoGa or ε-NiIn by low pressure metal–organic chemical vapor deposition [3]. However, it is usually impossible to grow thin films with a metal ratio $[E]/[M] > 1$ from compounds of type I. Fraser et al. [4] have shown that such gallium-rich films can be obtained from mixed-metal precursors exhibiting an MGa_2 stoichiometry, but these precursor compounds contain the two metal atoms linked together by ancillary ligands, involving M–N and Ga–O bonds, without direct metal-to-metal bonds (type II compounds). This caused severe incorporation of impurities into the deposited thin films (up to 20 at.% O) even in the presence of hydrogen as reducing carrier gas. We therefore aimed at volatile compounds of type III, $L(CO)_nM[ER_2(Do)]_2$, with an MGa_2 stoichiometry which contain the metals linked by M–Ga bonds rather than by ancillary bridging ligands.

2. Results and discussions

To the best of our knowledge there was only one single compound of this kind in the literature: *cis*-$[(CO)_4Fe]\{(\mu\text{-}Cl)InR^1\}_2$ ($R^1 \equiv C(SiMe_3)_3$), which was obtained from the reaction of $[(CO)_4Fe]Na_2$ with Cl_2InR^1 [5]. Following this strategy we treated a suspension of $[(CO)_4Fe]K_2$ in tetrahydrofuran (THF) with two equivalents of $ClGa[(CH_2)_3NMe_2](R)$ ($R \equiv {}^tBu$ or Ph) at room temperature (Scheme 1). Within 1 h, an only slightly cloudy pale-yellow solution was formed. The pattern of the $\nu(CO)$ absorptions of the reaction solution suggested the presence of a $(CO)_4M{-}L$ unit of local C_{3v} symmetry ($2A_1 + E$). Other structurally related compounds such as $(CO)_4Co{-}Ga[(CH_2)_3NMe_2](R)$ [6] exhibit very similar patterns, which are shifted to higher wavenumbers. From this we judged that the anionic intermediate $\{(CO)_4Fe{-}Ga[(CH_2)_3NMe_2](R)Cl\}^-$ had been formed, which could be isolated in a

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☆ Part X of the series Organo Group-13 Metal Complexes of d-Block Elements; for Part IX see Ref. [1].

* Corresponding author.

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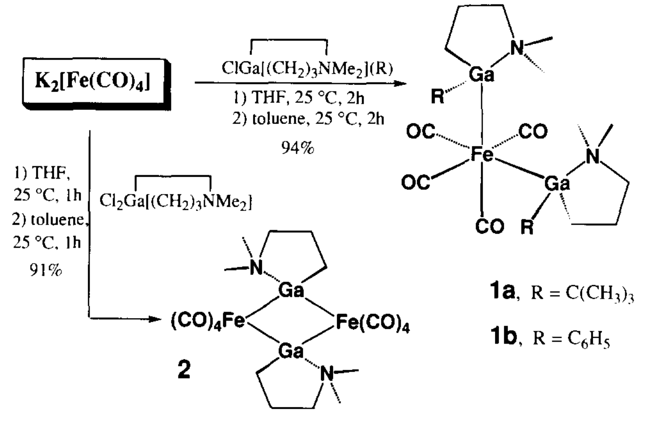

Scheme 1.

pure form as $[Ph_4As]\{(CO)_4Fe-Ga[(CH_2)_3NMe_2](R)-Cl\}$. The nucleophilicity of this anion is apparently too low to compete efficiently with the solvent and/or chloride ions which are present in the solution. Consequently the second Fe–Ga bond does not form under these conditions. This is a general problem when weakly nucleophilic carbonylmetallates are used in polar coordinating solvents to substitute the halide functionality at alkylgallium chlorides [7]. The replacement of the solvent THF by toluene afforded a nearly colorless solution and a white precipitate after an additional 2 h. From this solution, **1a** and **1b** were isolated upon crystallization almost quantitatively. Intramolecular base stabilization proved to be necessary for the success of this synthesis. With simpler alkyl gallium halides, e.g. $Cl-GaR_2$ ($R \equiv$ methyl or ethyl) the known tetranuclear dimers $[(CO)_4Fe-GaR(THF)]_2$ [8] resulted, besides the respective homoleptic gallium alkyls GaR_3. Apparently the primary product $(CO)_4Fe[GaR_2(THF)]_2$ is unstable in these cases with respect to alkyl transfer. The related tin complex $(CO)_4Fe(SnMe_3)_2$ also eliminates $SnMe_4$ to give $[(CO)_4Fe-SnMe_2]_2$ [9]. The compounds **1a** and **1b**, however, are completely stable against alkyl exchange or alkyl transfer in solution. This is different for the related Fe–In compound $(CO)_4Fe\{In[(CH_2)_3NMe_2]_2\}_2$ which eliminates $In[(CH_2)_3NMe_2]_3$ to give $\{(CO)_4Fe-In[(CH_2)_3NMe_2]\}_2$ [10]. The structure of **1a** and **1b** in solution can be deduced from the IR and NMR spectra. At low temperatures the fluxionality around the Ga center is partly frozen, thus leading to two signals for the diastereotopic $N-CH_3$ groups in the ^{13}C NMR spectrum. The $\nu(CO)$ IR pattern agrees with a *cis*-$(CO)_4FeL_2$ structure which can also be seen on comparison with the respective spectra of $[(CO)_4Fe-Ga(\eta^1-C_2H_3)(THF)]_2$ [8] and $\{(CO)_4Fe-Ga[(CH_2)_3NMe_2]\}_2$ (**2**) (Fig. 1). Also the ^{13}C NMR spectra of **1a** show the expected two resonances for *cis* and *trans* Ga–Fe–CO units at 217.2 and 218.4 ppm. At low temperatures the signal set for the 3-dimethylaminopropyl moiety is doubled in the ^{13}C NMR spectra of **1a** and **1b**. This is probably due to some isomers which can be resolved on the NMR time scale under this condition. It is difficult to distinguish between *cis* and *trans* isomers at the octahedral $(CO)_4FeL_2$ complex as one possibility and diastereomers as the other

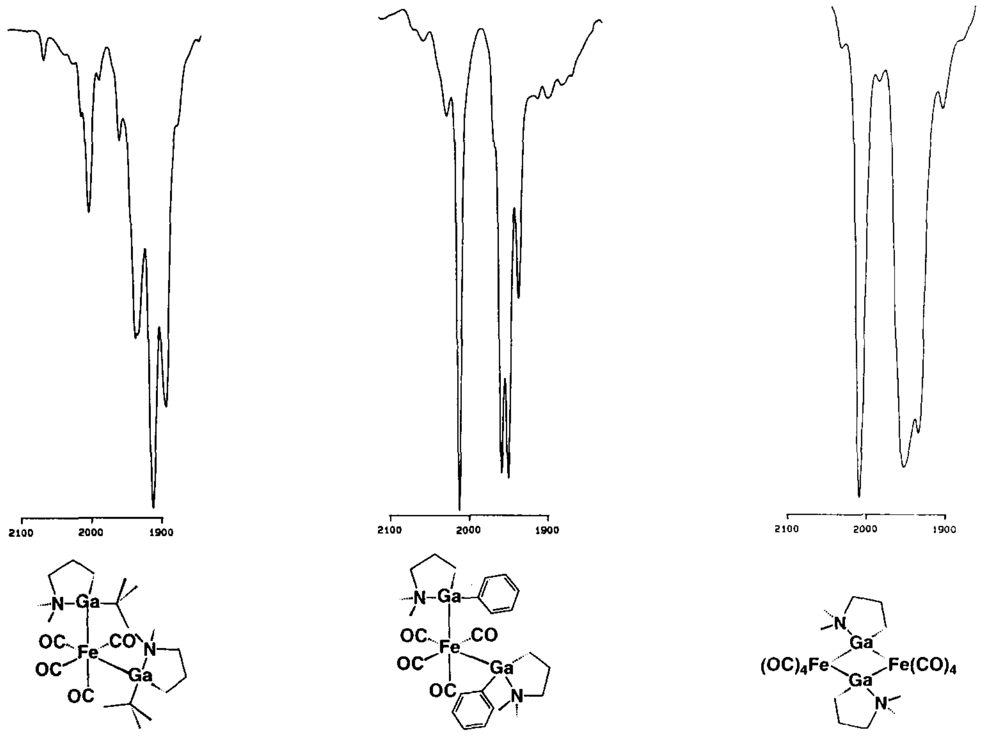

Fig. 1. Solution IR spectra of **1a**, **1b** and **2** in the carbonyl region (2100–1900 cm^{-1}) obtained in a CaF_2 cell (toluene: 25°C; $c \approx 0.1$ mol l^{-1}).

possibility (**1a** and **1b** exhibit two asymmetric Ga centers). At room temperature the ^{1}H and ^{13}C NMR spectra of **1a** and **1b** show only a single set of signals for the 3-dimethylaminopropyl moiety and the diastereotopic nature of the CH_2 and the N–CH_3 groups is no longer resolved. The electron impact and chemical ionization (isobutane) mass spectra of **1a** and **1b** do not show the molecular ion. The splitting of the Fe–Ga bonds is apparently preferred, which leads to intense peaks of $\{Ga[(CH_2)_3NMe_2](^tBu)^+\}$ with $m/z = 212$. Also alkyl transfer is observed as indicated by the peak at $m/z = 241$ which corresponds to $\{Ga[(CH_2)_3NMe_2]_2^+\}$. However, fragments with the correct isotope pattern for $FeGa_2$ are observed, too. **1a** crystallizes from *n*-heptane solutions as large well-shaped colorless crystals in the chiral orthorhombic space group $P2_12_12_1$ with the cell parameters $a = 11.833(1)$ pm, $b = 13.333(1)$ pm and $c = 17.437(2)$ pm, but the structure solution failed because of extensive disordering effects, which agrees well with the fluxionality of the system in solution. Currently we are trying to obtain single crystals of other $FeGa_2$ derivatives, e.g. **1b**, which may be better suited to X-ray analysis.

Reflective, metallic and adherent (tape test) thin films were grown by low pressure chemical vapor deposition at a substrate temperature of 200(±10)°C (rate, 0.1 μm h^{-1} and 0.1–0.01 Pa. The films were examined by scanning electron microscopy–energy-dispersive X-ray analysis (EDXA) and spectroscopy and proved to be uniform in the composition (Auger electron spectroscopy (AES) depth profiling at various positions; lateral resolution, 500 Å). The Ga-to-Fe metal ratio was measured by various techniques giving the following results: 1.9(±0.1) (atomic absorption spectroscopy; after dissolution of the films in aqueous nitric acid), 1.6(±0.2) (AES) and 2.0(±0.2) (EDXA). The films are thus gallium rich and the stoichiometry is very close to the limiting value of 2, as expected. The obtained films were rather pure; impurities of C and N were both very close or even below the AES detection limit and the oxygen content was low, near 4–5 at.% (Fig. 2).

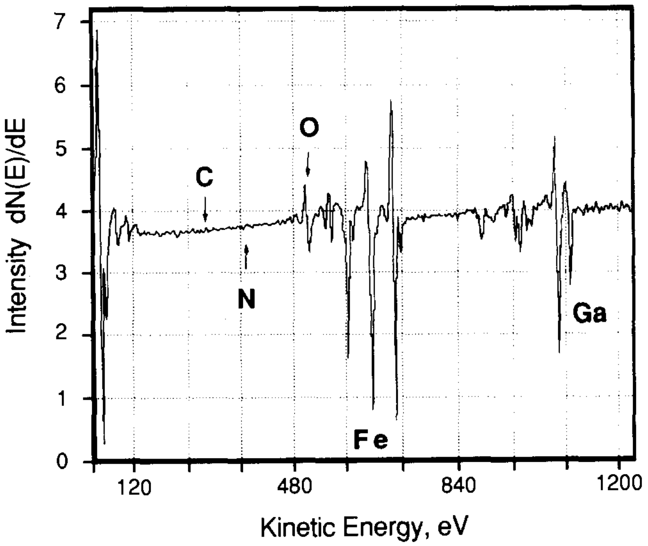

Fig. 2. Auger electron spectrum of an Fe–Ga alloy film 1.1(2) μm thick grown from precursor **1a** at 200 (±20)°C and 0.1 mTorr on a quartz slide after removal of surface contaminations with argon ion sputtering (2 min). The composition calculated from the spectrum using standard sensitivity factors [11] is as follows: Fe, 37(1) at.%; Ga, 57(1) at.%; C, 1(1) at.%; O, 3(1) at.%; N, much less than 1 at.%.

3. Experimental section

All manipulations were undertaken utilizing special reaction vessels [1] and glove-box techniques under an inert gas atmosphere (purified argon) using carefully dried (less than 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 residual protic impurities of the internal solvent and corrected to tetramethylsilane ($\delta = 7.15$ ppm for C_6D_6). For further information concerning experimental and analytical techniques see [1]. The starting compounds $ClGa[(CH_2)_3NMe_2](R)$ [12] and $[(CO)_4Fe]K_2$ [13] were prepared according to literature procedures. Abbreviations are as follows: Me = CH_3, Et = C_2H_5, Ph = C_6H_5, ^tBu = *tert*-butyl. Elemental analysis were provided by the Microanalytic Laboratory of the Technical University at Munich.

3.1. cis-Bis[(3-dimethylaminopropyl)(tert-butyl)gallio](tetracarbonyl)iron (1a); cis-bis[(3-dimethylaminopropyl)(phenyl)gallio](tetracarbonyl)iron (1b) and bis{[(3-dimethylaminopropyl)gallio](tetracarbonyl)iron} (2)

To a suspension of 830 mg (3.4 mmol) of $[(CO)_4Fe]K_2$ in 50 ml or THF, 1.67 g (6.8 mmol) of $ClGa[(CH_2)_3NMe_2](^tBu)$ were added with vigorous stirring. After 1 h the solvent was removed by vacuum distillation at room temperature. Then 50 ml of toluene were condensed onto the obtained yellow–orange residue. The mixture was stirred again for additional 2 h. After this the solvent was removed by vacuum distillation and the residue was extracted three times with 20 ml of *n*-heptane. The extracts were combined and filtered. Compound **1a** was obtained in an analytically pure form as large colorless crystals by slow evaporation of the solvent at room temperature (yield, 1.9 g (94%)), **1b** was prepared analogously from 641 mg (2.6 mmol) $[(CO)_4Fe]K_2$ and 1.4 g (5.2 mmol) $ClGa[(CH_2)_3NMe_2](Ph)$ (yield, 1.5 g (91%)). **2** was prepared analogously from 740 mg (3.0 mmol) $[(CO)_4Fe]K_2$ and 680 mg (3.0 mmol) $Cl_2Ga[(CH_2)_3NMe_2]$ (yield, 0.93 g (96%)).

1a: colorless crystals; melting point (m.p.) (decomposition), 98°C; sublimation, 90°C, 0.1 Pa. ^{1}H NMR (H,H-COSY, 399.78 MHz, toluene-d_8, −50°C): δ 0.98–1.12 (AA′BB′, 2H, $\mathrm{GaCH_2}$), 1.27–1.36 and 1.58–1.67 (AA′BB′CC′, 2H, $\mathrm{GaCH_2C}H_2$), 1.34 (s, 9H, $\mathrm{CCH_3}$), 1.95–2.08 (AA′BB′, 2H, $\mathrm{CH_2N}$), 2.02 and 2.13 (s, 6H, $\mathrm{NCH_3}$) ppm. $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (67.9 MHz, toluene-d_8, 25°C): δ 12.4 ($\mathrm{GaCH_2}$), 23.1 ($\mathrm{GaCH_2}C\mathrm{H_2}$), 28.8 (GaC), 30.6 ($C\mathrm{CH_3}$), 46.3 and 47.8 ($\mathrm{NCH_3}$), 65.3 ($\mathrm{CH_2N}$), 217.4 and 218.1 (FeCO) ppm. $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (67.9 MHz, toluene-d_8, −50°C): δ 11.9 and 12.1 ($\mathrm{GaCH_2}$), 22.8 and 23.0 ($\mathrm{GaCH_2}C\mathrm{H_2}$), 28.3 and 28.5 (GaC), 30.5 and 30.7 ($C\mathrm{CH_3}$), 45.8, 45.9 and 47.6, 47.7 ($\mathrm{NCH_3}$), 64.8 and 65.1 ($\mathrm{CH_2N}$), 217.2 and 218.4 (FeCO) ppm. IR (n-heptane): ν(CO) 2001 (m), 1935 (s) 1912 (vs) 1893 (vs) cm^{-1}. Anal. Found: C, 44.34; H, 6.48; N, 4.66; Fe 9.69, Ga, 22.53. $\mathrm{C_{22}H_{42}FeGa_2N_2O_4}$ Calc.: C, 44.49; H, 7.12; N, 4.71; Fe, 9.40; Ga, 23.48%.

1b: colorless crystals: m.p. (decomposition), 145°C; sublimation, 105°C, 0.1 Pa. ^{1}H NMR (399.78 MHz, toluene-d_8, 25°C): δ 0.82 (t, 2H, ^3J(H, H) = 7.3 Hz, $\mathrm{GaCH_2}$), 1.56 (s, 6H, $\mathrm{NCH_3}$), 1.62 (quint, 2H, ^3J(H, H) = 7.3 Hz, $\mathrm{GaCH_2C}H_2$), 1.81 (t, 2H, ^3J(H, H) = 7.3 Hz, $\mathrm{CH_2N}$), 7.20–7.32 (m, 3H, aromat.), 7.74 (m, 2H, aromat.) ppm. $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (67.9 MHz, toluene-d_8 25°C): δ 3.5 ($\mathrm{GaCH_2}$), 24.2 ($\mathrm{GaCH_2}C\mathrm{H_2}$), 46.9 ($\mathrm{NCH_3}$), 64.3 ($\mathrm{CH_2N}$), 127.6 ($p$-$\mathrm{C_6H_5}$), 127.8 ($o$-$\mathrm{C_6H_5}$), 137.6 ($m$-$\mathrm{C_6H_5}$), 149.1 (GaC) ppm, FeCO not observed. IR (n-pentane): ν(CO) 2012 (vs), 1959 (vs), 1950 (vs), 1937 (m) cm^{-1}.

2: yellow crystals: m.p. (decomposition), 186°C; sublimation 110°C, 0.1 Pa. $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (67.9 MHz, toluene-d_8, 25°C): δ 23.1 ($\mathrm{GaCH_2}$), 23.3 ($\mathrm{GaCH_2}C\mathrm{H_2}$), 47.7 ($\mathrm{NCH_3}$), 64.9 ($\mathrm{CH_2N}$); 211.4, 212.3, 213.8 (FeCO) ppm. IR (toluene): ν(CO) 2009 (vs), 1952 (vs), 1934 (vs) cm^{-1}. Anal. Found: C, 32.40; H, 3.84; N, 4.40 $\mathrm{C_{18}H_{24}Fe_2Ga_2N_2O_8}$ Calc.: C, 33.39; H, 3.74; N, 4.33%.

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