DOI: 10.1002/ejic.201100281

Chromium, Iron and Cobalt Carbonyl Complexes with Gallium Halides: Synthesis and Structures

Tobias Adamczyk,[a] Guang-Ming Li,[a] Gerald Linti,*[a] Hans Pritzkow,[a] Annekathrin Seifert,[a] and Thomas Zessin[a]

Keywords: Gallium / Iron / Chromium / Cobalt / Structure elucidation

The reactions of gallium subhalides Ga_2X_4·2dioxane (X = Cl, Br) and "GaI" with carbonylmetallates of chromium, iron and cobalt result in the formation of various gallium halide complexes. These are $[(CO)_5CrGaBr(thf)_2]$ (**6**), with a terminal GaX unit, and $[(CO)_4FeGaCl(thf)]_2$ (**1**), $[(CO)_4FeGaCl_2Na(thf)_2]_x$ (**2**), $[(CO)_4FeGaI_2Na(thf)_3]_2$ (**4**) and $[Cr_2(CO)_8(GaI_2)INa_2(thf)_7]_x$ (**8**) with GaX units in the bridging positions of gallium–transition-metal rings. In addition, mixed cyclic gallium–iron hydroxides $[\{(CO)_4Fe\}_2Ga_4Cl_5(OH)_3(thf)]$ **3** and **4** and gallium oxo/hydroxo cages **5**, **9** and **10** were observed. Rings of $[\{GaCo_4(CO)_{14}\}K(thf)]_6$ (**11**), prepared from $Ga_4Cl_4R_4$ [R = $Si(SiMe_3)_3$] and $K[Co(CO)_4]$, are connected through isocarbonyl–potassium interactions to form channels. All compounds were characterized spectroscopically and by X-ray crystallography. DFT calculations were performed on cobalt–gallium complexes to evaluate their bonding properties.

Introduction

Compounds with bonds between atoms of heavier group 13 elements, here confined to gallium, and transition-metal centres have gained increasing interest in recent years and the area has been reviewed from several points of view.[1–7] These complexes have been investigated as single-source precursors in metal–organic chemical vapour deposition (MOCVD)[1] or their examination was stimulated by the analogy between CO and RGa ligands. With RGa in terminal and bridging positions, the s-type lone-pair and empty π-type orbitals at the gallium atom in RGa [R = Cp*, $C(SiMe_3)_3$, $C(SiMe_3)_3$, tmp (tmp = 2,2,6,6-tetramethylpiperidino) and others][6,8–12] allow, in principle, σ-donor and π-acceptor properties. In particular, the controversy surrounding the bonding of terminal gallylene ligands has been discussed.[13–16] The isolation of [(CO)$_4$FeGa(aryl)] [aryl = 2,6-(2,4,6-iPr$_3$C$_6$H$_2$)$_2$C$_6$H$_3$] with a short gallium–iron bond (d_{Ga-Fe} = 222.5 pm) initiated the debate.[17] The analogous GaCp* complex has a longer Ga–Fe bond (d_{Ga-Fe} = 227.7 pm).[8] It has been emphasized that short bond lengths do not necessarily correlate to higher bond orders. Thus, quantum chemical calculations show some π-bonding in gallium–metal bonds, but the main contribution is a σ-donor bond from gallium to iron. The low coordination number of the gallium atom and the high polarity of the bond have been given as reasons for the short bonds. On the other hand, substituents on the gallium and transition-metal atoms influence the bonding properties. Gallium halide ligands are of interest because of their functionality. Complexes with GaCl can be synthesized only with the coordination of an additional Lewis base.[1] Examples are [(CO)$_4$FeGaCl(tmeda)] and [(CO)$_5$CrGaCl(tmeda)] (tmeda = N,N,N',N'-tetramethylethylenediamine) with long gallium–metal bonds relative to [(CO)$_5$CrGa(tmp)].[12] Only recently, the iron complex $[Cp^*Fe(dppe)(GaI)]^+[BAr^F_4]^-$ [Cp* = C_5Me_5, dppe = 1,2-bis(diphenylphosphanyl)ethane, Ar^F = 3,5-$(CF_3)_2C_6H_3$] with GaI as a CO analogue ligand was prepared.[18] The Ga–Fe bond length is similar to that in the Ga(aryl) complex mentioned above. $[(Cp^*Ga)_4Rh(GaCH_3)]^+[BArF_4]^-$[19] demonstrated that small organyl ligands like methyl are possible for terminal RGa ligands. Even complexes with naked Ga^+ ions were accessible.[20] In the homoleptic nickel complexes $[Ni\{GaC(SiMe_3)_3\}_4]$[10,21] and $[Ni_2(Gatmp)_7]$,[12] enhanced π-bonding might be observable.

Methods for their synthesis involve, for example, reactions of gallium(I) sources RGa (R = Cp*, $C(SiMe_3)_3$, tmp, nacnac {= $[N(dipp)C(Me)]_2CH$}) with reactive metal complexes,[2,22–24] reactions of carbonylmetallates with derivatives of gallium(III) and gallium subhalides[1,9,25] and the insertion of metal fragments into gallium–gallium bonds.[26] A survey of structurally characterized complexes with gallium–iron, –chromium and –cobalt bonds, which are of relevance to this report, is presented in Table 1.

RGa units with bulky substituents, in many cases silyl groups, arrange to form a large variety of cluster compounds,[2,27–31] for example, R_4Ga_4, $[R_6Ga_9]^-$, R_6Ga_{10}, $[R_8Ga_{26}]^{2-}$, R_9Ga_9 and higher clusters up to Ga_{84}. These cluster compounds are obtained by reactions of gallium

---

[a] Universität Heidelberg, Anorganisch-Chemisches Institut,
Im Neuenheimer Feld 270, 69120 Heidelberg, Germany
Fax: +49-6221-546617
E-mail: gerald.linti@aci.uni-heidelberg.de

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201100281.

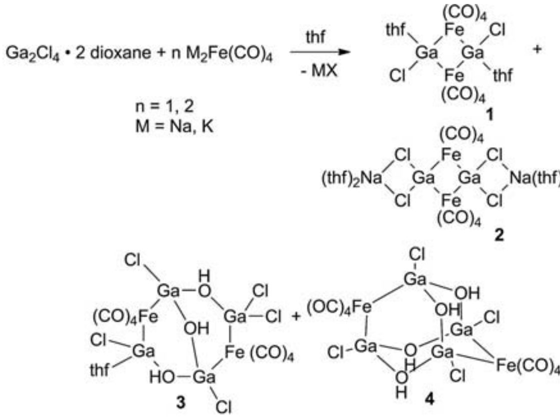
Table 1. Ga–M bond lengths and $\tilde{\nu}_{CO}$ values for selected structurally characterized complexes with Ga–Fe, Ga–Cr and Ga–Co bonds.

Complexes	d(Ga–M) [pm]	$\tilde{\nu}_{CO}$ [cm^{-1}]	Ref.
$[(CO)_4FeGaAr^*]$	222.48	2032 (s), 1959 (s), 1941 (vs), 1929 (vs)	[34]
$[(CO)_4FeGaCp^*]$	227.71	2037 (s), 1966 (s), 1942 (vs)	[8]
$[Cp(CO)_2FeGaS]_2$	233.7	2001 (s),1993 (vs), 1976 (vs), 1923 (vs), 1986 (vs)	[35]
$[(CO)_4FeGaCl(tmeda)]$	233.78	2011 (vs), 1928 (vs),1881 (vs)	[1]
$[Cp(CO)_2FeGaCl_2(NMe_3)]$	236.18	1989 (vs), 1934 (vs)	[36]
$[Cp(CO)_2FeGaCl_2(thf)]$	231.7(1)	1990 (s), 1995 (s)	[37]
$[Cp(CO)_2FeGa(R^N)(BH_4)]$	237.5	1975 (vs), 1920 (vs)	[38]
$[Fe_2(CO)_6\{\mu\text{-}GaSi(SiMe_3)_3\}_3]$	238.18	1964 (s), 1921 (s)	[9]
$[Fe_2(CO)_6\{\mu\text{-}GaC(SiMe_3)_3\}_3]$	242.2(1)	1973 (s), 1937 (s), 1922 (m)	[39]
$[\{Cp(CO)_2Fe\}_2Ga(t\text{Bu})]$	240.6, 241.6	1978 (vw, sh), 1967 (vs), 1927 (vs), 1915 (vw)	[40]
$[\{Cp(CO)_2Fe\}_2GaCl]$	235.24(4)	1955 (s), 1932 (s), 1919 (sh)	[30,31]
$[\{Cp(CO)_2Fe\}_2Ga]^+$	227	2016 (m), 1994 (s), 1963 (s)	[30,31]
$[\{Cp(CO)_2Fe\}_2GaCl(thf)]$	239.0(1)	1992 (s), 1982 (s), 1971 (s), 1936 (s)	[37]
$[(CO)_4FeGa(Me)Fe(CO)_4]^{2-}$	241.58	1952 (vs), 1874 (vs, sh), 1851 (vs), 1827 (vs, sh)	[41]
$[Cp(CO)_2FeGa(\eta^1\text{-}C_5H_4Me)_2(NC_5H_5)]$	242.72	–	[32]
$[\{Cp(CO)_2Fe\}_3Ga]$	243.6–245.6	1987 (m), 1965 (s), 1929 (s)	[42]
$[(CO)_4FeGa(\eta^1\text{-}C_2H_3)(thf)]_2$	251.0	–	[43]
$[(CO)_5CrGaCp^*]$	240.46(7)	2052 (s), 982 (s), 1918 (vs), 902 (vs)	[8]
$[(CO)_5CrGaC_4H_2(t\text{Bu})_2P]$	239.0(1)	2022 (m), 1936 (sh), 1870 (s)	[44]
$[(CO)_5CrGaCl(tmeda)]$	245.6(1)	2033 (s), 1947 (s), 1900 (vs)	[45]
$[(CO)_5CrGaCH_3(tmeda)]$	247.9(1)	2013 (vs), 1920 (s), 1844 (vs)	[46]
$[(CO)_5CrGaCl_2(thf)_2]$	–	2035 (m), 1955 (w), 1913 (vs)	[45]
$[(CO)_6Co_2(GaCp^*)_2]$	238.8	2023, 1989, 1953, 1948	[8]
$[(CO)_6Co_2(Gatmp)_2]$	234.7(1)–239.1(1)	2046, 2007, 1974, 1863	[12]

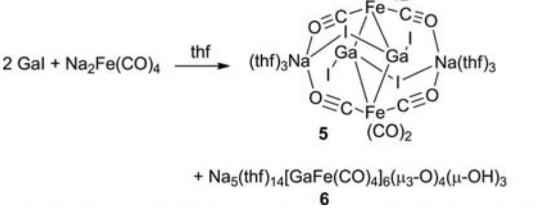
subhalides with the corresponding metallated silanides. To explore the possibility of using metallo-organic substituents to stabilize gallium cluster compounds, the gallium subhalides Ga_2X_4·2dioxane (X = Cl, Br) and "GaI"[32] as well as $Ga_4Cl_4R_4$ [R = $Si(SiMe_3)_3$][33] and Ga(nacnac)[24] were treated with carbonylmetallates and carbonyls of chromium, iron and cobalt. Herein we describe the formation of several gallium–metal complexes obtained from these reactions, which were performed by redox disproportionation of gallium instead of by the stabilization of gallium in a low oxidation state and the formation of cluster compounds.

Results and Discussion

Starting from gallium subhalides we prepared several $CpFe(CO)_2$–gallium complexes.[37] $Na_2[Fe(CO)_4]$ reacted with the gallium(II) chloride Ga_2Cl_4·2dioxane at low temperature in a complex way. A combination of substitution and redox reactions yielded the orange-coloured gallium–iron ring compounds **1** and **2** accompanied by colourless **3** [Equation (1)]. If $K_2[Fe(CO)_4]$ was used instead, **4** was obtained. The formation of **3** and **4** might be due to hydroxide impurities in $M_2[Fe(CO)_4]$. The ratio of gallium halide to carbonylmetallate influenced the products formed: in a 1:2 ratio, products **1** and **4** were formed, whereas in a 1:1 ratio, **2** and **3** were formed. Both **1** and **2** have an Fe_2Ga_2 core, **3** and **4** an Fe_2Ga_4 core. The only difference lies in the additional coordination of NaCl (**1** and **2**) or the ratio of OH/Cl (**3** and **4**). This is an additional hint of hydroxide impurities as the source of the hydroxo groups.



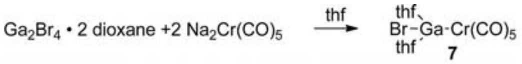
(1)



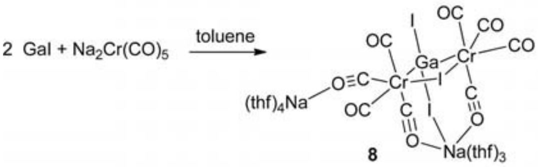
(2)

When 2 equiv. of freshly prepared "GaI" were treated with $Na_2[Fe(CO)_4]$, the gallium–iron ring compound **5** was formed together with the gallium oxo/hydroxo cage **6** [Equation (2)]. A closely related Ga_2Fe_2 ring compound, $[(C_2H_3)(thf)GaFe(CO)_4]_2$, was synthesized starting from $EtGaCl_2$.[43]

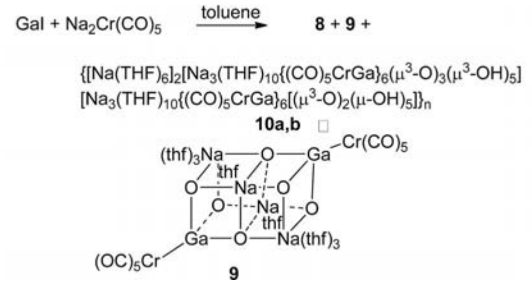
When $Na_2[Cr(CO)_5]$ was treated with the gallium(II) bromide Ga_2Br_4·2dioxane in a 2:1 ratio, the terminal GaBr(thf)$_2$–chromium complex **7** was obtained [Equation (3)]. The homologous [GaCl(thf)$_2$] complex is accessible from



$$\mathrm{Ga_2Br_4\cdot 2\,dioxane} + 2\,\mathrm{Na_2Cr(CO)_5} \xrightarrow{thf} \mathrm{Br{-}Ga(thf)_2{-}Cr(CO)_5}\ \mathbf{7} \qquad (3)$$



(4)

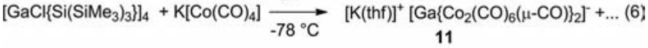


(5)

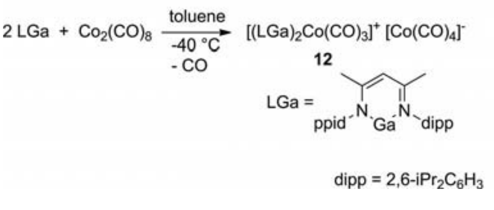
K$_2$[Cr(CO)$_5$] and GaCl$_3$.[45] Starting from “GaI”, the binuclear gallium–chromium complex **8** was isolated [Equation (4)]. In the latter, two chromium centres are connected through a [GaI$_2$]$^-$ and an I$^-$ bridge. In addition, the Cr(CO)$_5$-substituted gallium–oxo cages **9** and **10** were obtained if a 1:1 stoichiometry was used [Equation (5), see the Supporting Information]. Their formation hints at a high hydroxide content in K$_2$[Cr(CO)$_5$].

The dimeric functional digallane Ga$_4$Cl$_4$R$_4$ [R = Si(SiMe$_3$)$_3$] reacted with K[Co(CO)$_4$] in a complex manner [Equation (6)]: [RGaCo(CO)$_4$]$_2$, the substitution product, was not observed. Instead, the gallium carbonylcobaltate [K(thf)]$_6$[Ga{Co$_2$(CO)$_6$(μ-CO)}$_2$]$_6$ (**11**) was obtained in low yield. Gallium–iron cluster compounds with bridging GaSi(SiMe$_3$)$_3$ ligands[9] were prepared from the reaction of this digallane with carbonylferrates with the preservation of the gallium–silicon bond. On the other hand, [Cp*GaCl$_2$] reacted with K[Co(CO)$_4$] with loss of the Cp* group to give [Ga{Co$_2$(CO)$_7$}$_2$]$^-$.[47,48] With different cations, namely [K(toluene)$_2$]$^+$ and [Li(thf)]$^+$, dimers and chained polymers of this unit were obtained.

[Co$_2$(CO)$_8$] was heterolytically cleaved by Ga(nacnac) [GaL; Equation (7)] to give [(LGa)$_2$Co(CO)$_3$]$^+$[Co(CO)$_4$]$^-$ (**12**). This is comparable to the oxidative addition reactions of H$_2$, E–H[49] and E–X[50] bonds to Ga(nacnac).



$$\mathrm{[GaCl\{Si(SiMe_3)_3\}]_4} + \mathrm{K[Co(CO)_4]} \xrightarrow[-78\ ^\circ C]{thf} \underbrace{\mathrm{[K(thf)]^+\,[Ga\{Co_2(CO)_6(\mu\text{-}CO)\}_2]^-}}_{\mathbf{11}} + \ldots \qquad (6)$$



(7)

IR Spectroscopic Characterization

The IR spectra of **1**, **2** and **5** show the four CO stretching modes typical of *cis*-[L$_2$Fe(CO)$_4$] complexes. In the case of **4**, two broad bands hide weaker ones. Complex **5** exhibits the vibrations with lowest wavenumbers, which is in line with the isocarbonyl coordination of two of the CO groups to sodium.

The terminal GaBr complex **7** gives rise to three CO stretching modes ($\tilde{\nu}$ = 2061, 1989, 1911 cm^{-1}). These are at higher wavenumbers than those observed for [(CO)$_5$CrGaCl(thf)$_2$] and [(CO)$_5$CrGaCl(tmeda)]. This hints at Cr–C π-bonding weaker than that in **7**, which might be due to a less polar Ga–Cr bond as a consequence of the change of the halogen atom.

The IR spectrum of anionic **11** shows two bands in the CO stretching region, one at 1968 cm^{-1} for terminal carbonyls and one at 1764 cm^{-1} for the μ^2-bridging carbonyls. This indicates a weakening of the CO bond in comparison with neutral cobalt carbonyls like [Co$_2$(CO)$_8$] and [Co$_2$(CO)$_6$(GaCp*)$_2$]. [Co(CO)$_4$]$^-$ has an even weaker CO bond ($\tilde{\nu}$ = 1890 cm^{-1}).

For **12**, three strong IR absorptions are observed at 1941, 1857 and 1802 cm^{-1}, which indicates an [L$_2$Co(CO)$_3$] cation with a symmetry lower than D_{3h}, weakly π-accepting ligands L and a coordinating [Co(CO)$_4$]$^-$ anion.

Crystal Structure Analysis of the [XGaM(CO)$_n$] Complexes 1, 2, 5, 7 and 8

Complex **1** crystallizes in the monoclinic space group $P2_1/n$. The core of **1** (Figure 1) consists of a centrosymmetric planar Ga$_2$Fe$_2$ ring. The bond angles of the inner ring are wide [108.74(2)°] at the gallium atoms and acute [71.26(2)°] at the iron atoms. The gallium atoms are tetracoordinated by the two iron atoms, a chlorine atom and a thf ligand. The GaCl and GaO bond lengths [d_{GaCl} = 222.9(1) pm, d_{GaO} = 202.9(3) pm] are in the normal range for these bonds. The GaFe bonds [d_{GaFe} = 246.59(7), 247.86(7) pm] in **1** are shorter by 5 pm than those in [(CO)$_4$FeGa(C$_2$H$_3$)(thf)]$_2$, but longer than those in terminal GaCl(donor)$_2$ and GaR–iron complexes (Table 1), as expected. The iron atoms are in a distorted octahedral coordination sphere of four CO ligands and two gallium atoms.

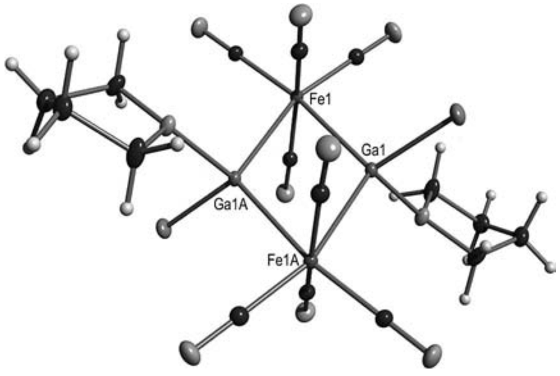


Figure 1. View of a molecule of **1**. Selected bond lengths [pm] and angles [°]: Ga(1)–Fe(1) 246.59(7), Ga(1)–Fe(1A) 247.86(7), Fe(1)–Ga(1)–Fe(1A) 108.74(2), Ga(1)–Fe(1)–Ga(1A) 71.26(2).

Complex **2** crystallizes in the triclinic space group $P\bar{1}$. It forms polymeric chains of fused Na$_2$Cl$_2$, NaCl$_2$Ga and

Ga_2Fe_2 rings (Figure 2a). The Ga_2Fe_2 ring core (Figure 2b) has similar bond lengths and angles to that in **1**. The gallium atoms are coordinated in a distorted tetrahedron by two iron atoms and two chlorine atoms. Complex **2** is the double $Na(thf)_2Cl$ adduct of $[ClGaFe(CO)_4]_2$. The GaCl bonds [d_{GaCl} = 226.4(1), 231.1(1) pm] are longer than those in **1**. The chlorine atoms coordinate to one or two sodium atoms. The different coordination numbers of two and three for these atoms cause the different Ga–Cl bond lengths. The sodium atoms linking the Ga_2Fe_2 rings are coordinated in a distorted trigonal bipyramid by three chlorine atoms and two thf molecules. A similar oligomer is formed by $[(CO)_4Fe(GaCl_2)_2](NaCl)_2{\cdot}2OEt_2$.[48]

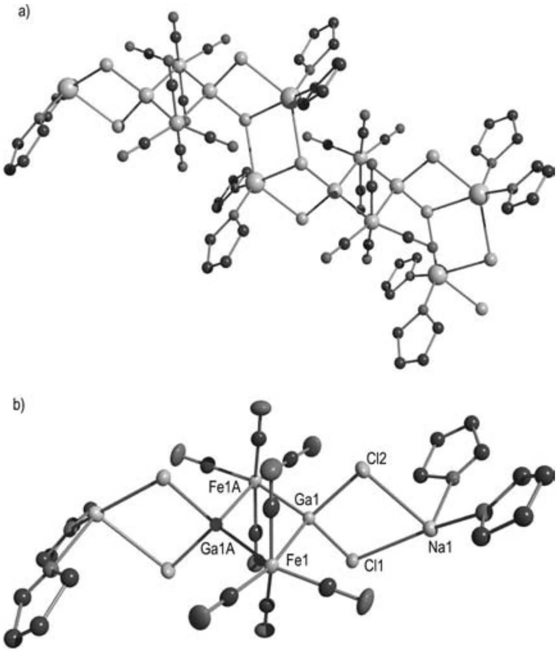


Figure 2. (a) View of the polymeric chains in **2**. (b) View of the $(NaCl_2GaFe)_2$ unit in **2**. Hydrogen atoms have been omitted for clarity. Selected bond lengths [pm] and angles [°]: Ga(1)–Fe(1A) 246.8(1), Ga(1)–Fe(1) 247.77(9), Cl(2)–Ga(1)–Cl(1) 95.72(4), Fe(1A)–Ga(1)–Fe(1) 108.37(3), Ga(1A)–Fe(1)–Ga(1) 71.63(3).

Complex **5** crystallizes in the triclinic space group $P\bar{1}$. It can be viewed upon as the $Na(thf)_3I$ adduct of $[IGaFe(CO)_4]_2$ (Figure 3). The central Ga_2Fe_2 ring has a similar shape to those in **1** and **2** with acute angles at the iron atoms and wide angles at the gallium atoms. The Ga–Fe distances [d_{GaFe} = 251.4(1) pm] are longer than in **1** and **2** but of the same length as those already mentioned in $[(CO)_4FeGa(C_2H_3)(thf)]_2$. This might be due to the lower electronegativity of iodine compared with chlorine. The Fe–Ga bond is longer by nearly 30 pm than in the cationic terminal GaI complex $[Cp^*Fe(dppe)(GaI)]^+$, which shows the influence of coordination numbers at gallium.[18]

In contrast to **2** the sodium atoms are coordinated in a distorted octahedron by three thf molecules, one iodine atom and two isocarbonyl interactions. These Na–OC bonds are significantly different [d_{NaO} = 272.2(6), 248.0(5) pm].

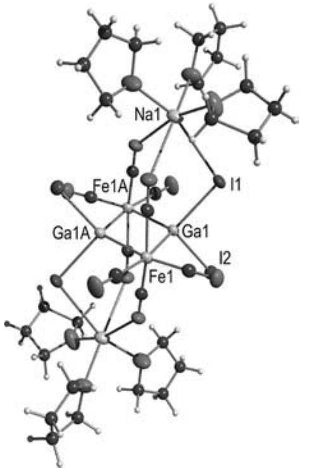


Figure 3. View of the molecule **5**. Selected bond lengths [pm] and angles [°]: Fe(1)–Ga(1) 251.1(1), Fe(1)–Ga(1A) 251.6(1), Ga(1)–Fe(1)–Ga(1A) 73.31(4), Fe(1)–Ga(1)–Fe(1A) 106.69(4), I(2)–Ga(1)–I(1) 97.62(4).

Complex **7**, crystallizing in the triclinic space group $P\bar{1}$ with two crystallographic independent molecules, is a monomeric $[(CO)_5CrGaBr(thf)_2]$ complex (Figure 4). The gallium atom is coordinated in a distorted tetrahedral manner by a chromium atom, a bromine atom and two thf molecules. The chromium atom is coordinated octahedrally by five CO groups and the gallium ligand. The GaCr bond [d_{GaCr} = 242.2(1) pm] is shorter than in $[(CO)_5CrGaCl(tmeda)]$ but longer than in $[(CO)_5CrGaCp^*]$.

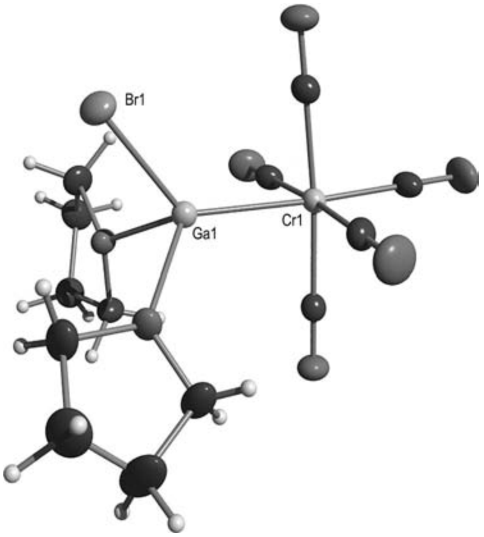


Figure 4. View of one of the two independent molecules of **7**. Selected bond lengths [pm] and angles [°]: Ga(1)–Cr(1) 242.20(9), Ga(1)–Br(1) 239.2(1), Br(1)–Ga(1)–Cr(1) 128.63(3).

Complex **8** crystallizes in the monoclinic space group $P2_1/n$. Here, the polymeric chain is made up of Cr_2GaI rings linked by sodium cations (Figure 5). The central unit is a trinuclear bis(chromium)gallium cluster in which the gallium atom is bonded to two iodine atoms and two $Cr(CO)_4$ units. These $Cr(CO)_4$ units themselves are linked through an iodine bridge. This dianionic monomer has two sodium counterions in different environments. One sodium atom is coordinated by three thf molecules, one gallium-bonded iodine atom and two "isocarbonyl" groups from both $Cr(CO)_4$ units. The other sodium atom has four thf ligands and two isocarbonyl contacts. As these CO groups belong to different Cr_2GaI rings, this sodium atom is the polymer linker. The central $[(CO)_4Cr]_2(\mu^2\text{-}GaI_2)(\mu^2\text{-}I)$ unit may be viewed as resulting from the condensation of a $[(CO)_5CrGaI_2]^-$ and a $[(CO)_5CrI]^-$ unit with loss of two CO. The Ga–Cr bonds [d_{GaCr} = 250.2(1) pm] are longer than those in other Ga–Cr complexes (see Table 1), but are reasonable in view of the long Cr–I bonds [$d_{Cr–I}$ = 271.0 pm], which are also part of the ring.

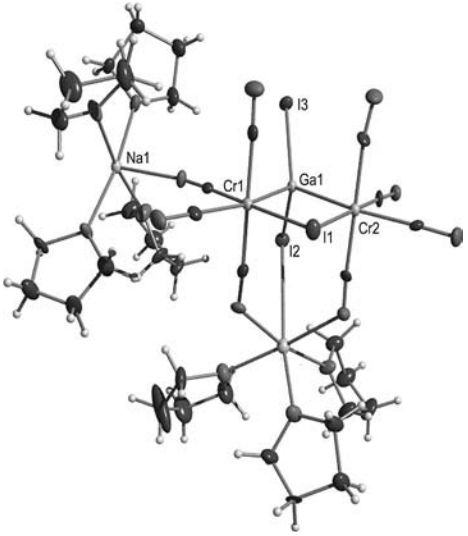


Figure 5. View of a building block of **8**. Selected bond lengths [pm] and angles [°]: Ga(1)–Cr(1) 249.7(1), Ga(1)–Cr(2) 250.6(2), Ga(1)–I(2) 264.1(2), Ga(1)–I(3) 262.4(2), I(1)–Cr(1) 270.5(2), I(1)–Cr(2) 271.5(2), I(3)–Ga(1)–I(2) 102.98(5), Cr(1)–I(1)–Cr(2) 69.64(5).

Crystal Structure Analysis of GaO Rings and Cages 3, 4 and 6

Complex **3** crystallizes with 3 equiv. of thf in the monoclinic space group $P2_1/n$ (Figure 6). Here, two boat-shaped Ga_3FeO_2 six-membered rings are fused to form a bicyclo[3.3.1]nonane-type structure. Both rings contain a $Fe(CO)_4Ga_2$ structural element with two GaCl units as the bridge heads. All gallium atoms are linked by μ^2-OH groups. The GaFe [d_{GaFe} = 238.45(8)–242.28(8) pm] and Ga–O bond lengths are in the range typical of these bonds. All the gallium atoms are tetracoordinated. Ga(1) is connected to an iron atom, one oxygen atom (OH), one chlorine atom and the oxygen atom of a thf molecule. Ga(2) bears two chlorine atoms instead of thf and Ga(3) and Ga(4) are bonded to iron and chlorine atoms and two oxygen atoms of OH groups.

Complex **4** (Figure 7) crystallizes as colourless needles in the triclinic space group $P1$. The crystals are very weakly diffracting and the quality of the structure does not allow discussion of its bond lengths. In the unit cell are two molecules of **4** together with seven thf molecules. There is no significant difference between the two independent molecules, but the seven thf molecules make the chosen space group plausible. The $Ga_4Fe_2O_4$ core of **4** adopts an adamantoidal structure in which the gallium atoms are in tetrahedral positions and the oxygen (OH) and iron atoms [$(FeCO)_4$] are μ^2-bridging.

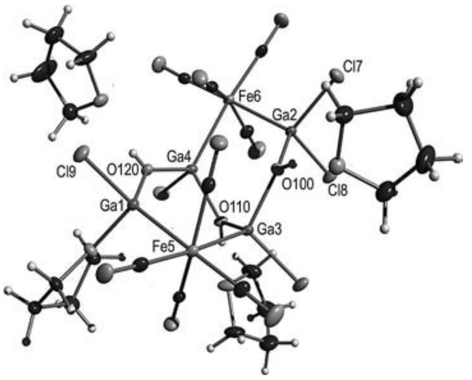


Figure 6. View of crystal structure of **3**. Selected bond lengths [pm] and angles [°]: Ga(1)–Fe(5) 238.45(8), Ga(2)–Fe(6) 242.28(8), Ga(3)–Fe(5) 241.73(8), Ga(4)–Fe(6) 239.94(6), Ga(1)–O(120) 186.7(2), Ga(1)–O(20) 199.9(2), Ga(2)–O(100) 190.3(2), Ga(3)–O(100) 187.7(2), Ga(3)–O(110) 189.4(2), Ga(4)–O(110) 189.8(2), Ga(4)–O(120) 190.1(2), O(110)–Ga(4)–O(120) 93.8(1), O(110)–Ga(4)–Fe(6) 119.22(7), Ga(1)–Fe(5)–Ga(3) 90.51(2), Ga(4)–Fe(6)–Ga(2) 88.90(2).

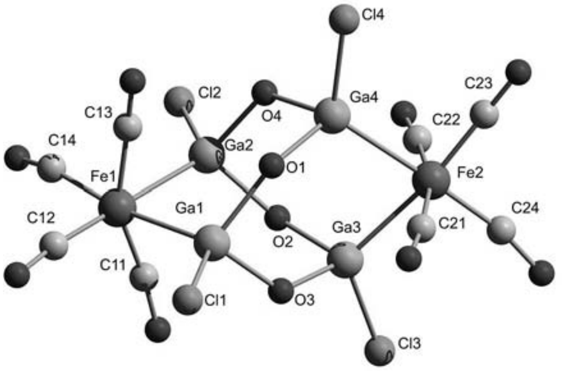


Figure 7. View of a molecule of **4**.

The Ga_6O_7 cage compound **6** (Figure 8a) crystallizes in the monoclinic space group $P2_1/n$ with a thf molecule. The gallium atoms are at the corners of an octahedron and are linked by μ^3-O atoms and μ^2-OH groups. The cage can be described as an incomplete Ga_3O_4 cubane in which the missing Ga corner is replaced by a $Ga_3(OH)_3$ ring in the chair conformation. Each gallium atom is bonded to an $Fe(CO)_4$ fragment. The gallium–iron bonds [d_{GaFe} = 234.3(1)–235.9(1) pm] are shorter than those in **3**. The non-bonded Ga–Ga distances are close to 290 pm, which is typical for Ga_2O_2 rings like $[tBu_2GaOtBu_2]$.[51–53]

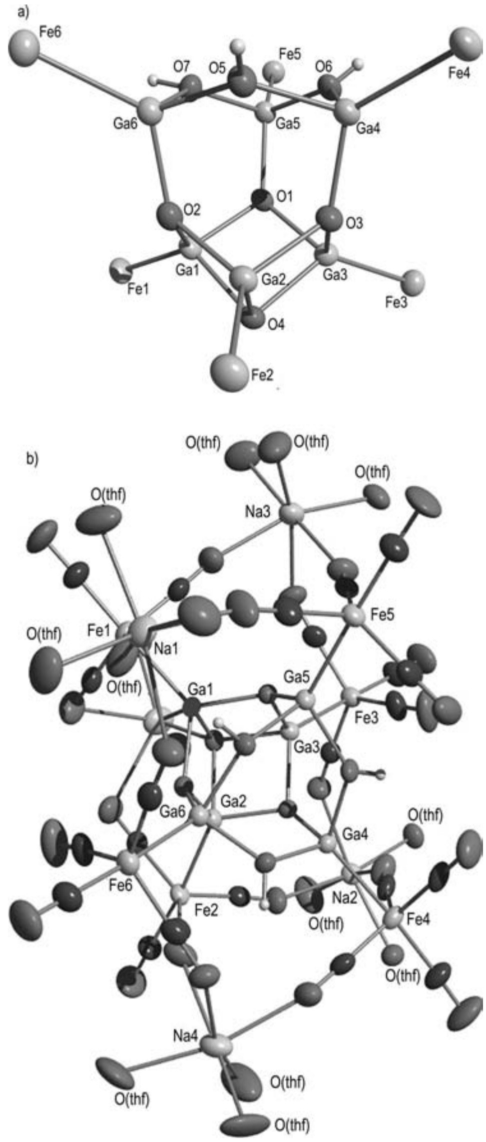


Figure 8. (a) FeGaO core of **6**. (b) View of **6** with Na(thf)$_3$ units [only the O atoms of the thf groups O(thf) are shown]. Selected bond lengths [pm]: Ga(1)–Fe(1) 234.6(1), Ga(2)–Fe(2) 234.4(1), Ga(3)–Fe(3) 234.3(1), Ga(4)–Fe(4) 235.9(1), Ga(5)–Fe(5) 234.26(9), Ga(6)–Fe(6) 235.3(1).

This core of **6** is five-fold negatively charged. This charge is balanced by five Na(thf)$_3$ units each of which are connected to the core by three isocarbonyl contacts (Figure 8b).

Common to **3**, **4** and **6** are direct Ga–Fe bonds with the oxygen atoms bridging two or three gallium atoms each. The Ga$_4$(Fe$_2$O$_4$) adamantoid cage is comparable to [(RGa)$_4$O$_6$H$_n$]^x adamantoidal cages [R = C(SiMe$_3$)$_3$, $n = 4$, $x = 0$;[54] R = Si(SiMe$_3$), $n = 5$, $x = 1+$][9]. The incomplete cubane part of **6** corresponds to gallaoxocubanes (RGaO)$_4$ [R = Si(CMe$_3$)$_3$.[55] Higher galliumoxo cages are [Mes$_6$Ga$_6$O$_4$(OH)$_4$],[56] [Mes$_6$Ga$_6$O$_4$F$_4$],[57] [MesGaO]$_9$[58] and [*t*Bu$_{12}$Ga$_{12}$O$_{10}$(OH)$_4$].[54,59] Complex **3**, which has a lower oxygen/gallium ratio, is comparable to [(RGa)$_3$Fe(CO)$_4$(OH)$_4$][9] and [{CpFe(CO)$_2$Ga}$_6$O$_4$(OH)$_2$I$_2$].[60]

Crystal Structure Analysis of Cobalt Complexes 11 and 12

Complex **11** crystallizes in the trigonal space group $R\bar{3}$. The supramolecular structure is made up of [Ga{Co$_2$(CO)$_7$}$_2$]$^-$ units linked by [K(thf)]$^+$ cations. In the subunits the gallium atom is coordinated in a tetrahedrally distorted manner by two bidentate [Co$_2$(CO)$_7$]$^{2-}$ ligands (Figure 9). The Ga–Co bonds ($d_{\text{Ga–Co}}$ = 237.1–244.0 pm) are different but in the usual range for [RGaCo$_2$(CO)$_7$] complexes.[8,12] The Co–Co distances ($d_{\text{Co–Co}}$ = 256.4, 257.0 pm) are only 4 pm larger than in [Co$_2$(CO)$_8$] but shorter by 26 pm than those in [GaRCo$_2$(CO)$_7$]. The bonding parameters are very similar to those described previously for M[Ga{Co$_2$(CO)$_7$}$_2$] [M = Li(thf), K(toluene)$_2$].[47,48]

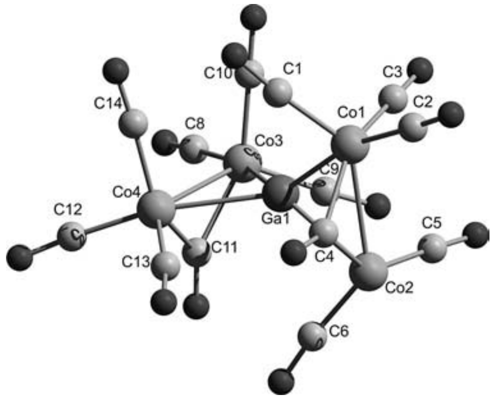


Figure 9. View of the GaCo$_4$ unit in **11**. Selected bond lengths [pm] and angles [°]: Ga(1)–Co(1) 237.08(9), Ga(1)–Co(3) 238.04(8), Ga(1)–Co(4) 243.18(8), Ga(1)–Co(2) 244.04(9), Co(2)–Co(1) 256.41(10), Co(4)–Co(3) 257.66(9), K(1)–O(15) 267.2(5), K(1)–O(4) 271.9(3), K(1)–O(13) 279.9(3), Co(1)–Ga(1)–Co(3) 138.47(3), Co(1)–Ga(1)–Co(4) 136.12(3), Co(3)–Ga(1)–Co(4) 64.74(3), Co(1)–Ga(1)–Co(2) 64.39(3), Co(3)–Ga(1)–Co(2) 136.07(3), Co(4)–Ga(1)–Co(2) 131.55(3), Ga(1)–Co(2)–Co(1) 56.49(2), Ga(1)–Co(4)–Co(3) 56.67(2), Ga(1)–Co(3)–Co(4) 58.60(2).

The main difference is in the type of aggregation: two GaCo$_4$ units are linked through the [K(thf)]$^+$ cations and the bridging and terminal carbonyls of each GaCo$_4$ unit through K–isocarbonyl contacts. Thus results a cyclic hexamer, which contains a benzene molecule in the centre (Figure 10). The pores of the rings, measured by the distance between opposite oxygen atoms, is 887 pm. Thus, a benzene molecule with a diameter of 460 pm fits in neatly.

The hexameric aggregates are stacked in the crystal to form channels (Figure 11). The rings are connected by additional K–CO contacts such that the potassium atoms are six-fold coordinated by a thf molecule and four isocarbonyl groups. In the staples, the rings are twisted against one another by 30° to form an ABAB staple.

Complex **12** crystallizes as yellow crystals in the space group $P\bar{1}$. It is an ionic compound with a tetrahedral [Co(CO)$_4$]$^-$ anion and a [(LGa)$_2$Co(CO)$_3$]$^+$ cation (Figure 12). In the cation a central cobalt atom is coordinated trigonal bipyramidally by three carbonyl groups and two galliumdiketoiminate ligands. The latter are in axial positions. The cobalt–carbon distances ($d_{\text{Co–C}}$ = 169.5 pm on average) are shorter than in the anionic part ($d_{\text{Co–C}}$ =

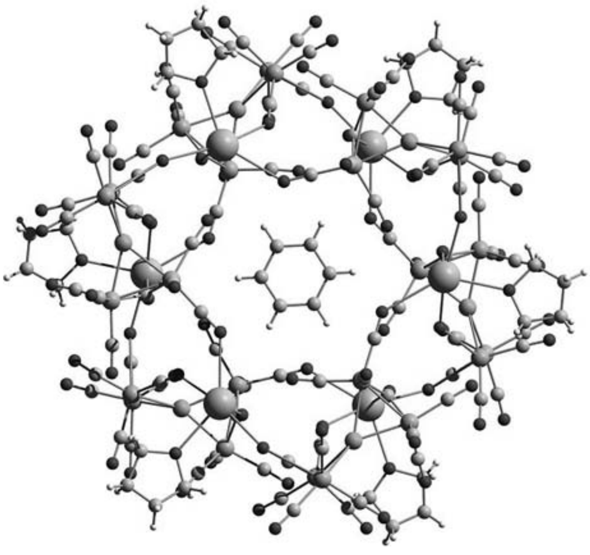


Figure 10. Hexameric rings of **11**.

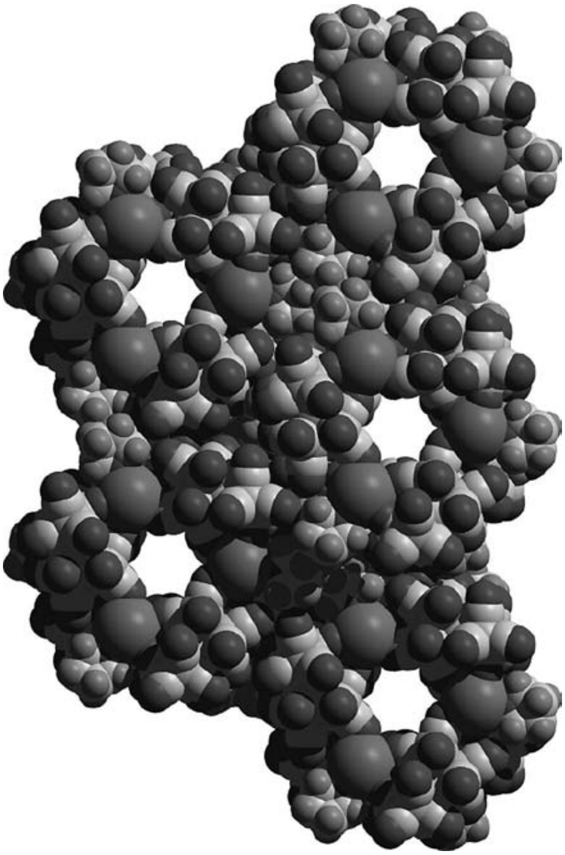


Figure 11. View of neighbouring tubes of **11** (benzene has been omitted for clarity).

174.1 pm on average). This indicates increased cobalt-to-carbon back-bonding because of the presence of σ-donating gallium ligands. The gallium–cobalt distances [$d_{Ga–Co}$ = 229.0(1), 232.4(1) pm] are shorter than those in [$Co_2(CO)_6(GaR)_2$] complexes with bridging GaR units [R = Cp*:[8] $d_{Ga–Co}$ = 237.84(5)–239.1(1) pm; R = tmp:[46] $d_{Ga–Ga}$ = 234.7(1)–239.1(1) pm] and in [$(CO)_4CoGaR_2(Do)$] complexes [$d_{Ga–Co}$ = 234.2–258.6 pm; Do = thf, pyridine].[61,62] This shows **1** to be a good σ-donor ligand towards metal complex fragments, as has been demonstrated previously.[63–65]

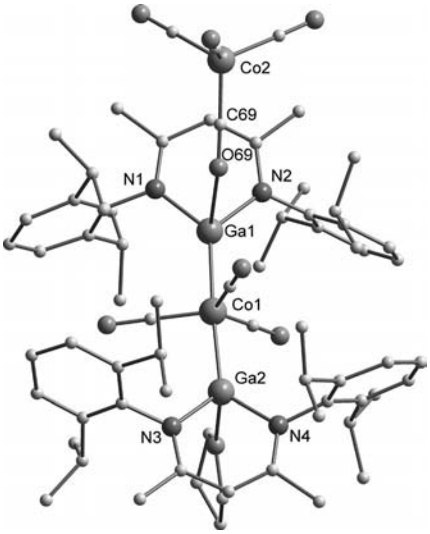


Figure 12. View of a molecule of **12**. Hydrogen atoms have been omitted for clarity. Selected bond lengths [pm] and angles [°]: Co(1)–C(65) 168.1(9), Co(1)–C(64) 169.7(1), Co(1)–C(63) 170.5(7), Co(1)–Ga(1) 228.9(1), Co(1)–Ga(2) 232.4(1), Ga(1)–N(2) 190.2(7), Ga(1)–N(1) 192.0(7), Ga(2)–N(3) 193.8(7), Ga(2)–N(4) 195.3(7), Ga(1)–O(69) 266.5(5), Ga(2)–O(1) 220.6(5), Ga(1)–Co(1)–Ga(2) 176.6(6).

The two gallium heterocycles are nearly planar. The gallium–nitrogen distances are in the range 190.2–195.3 pm. The shorter ones are located in the ring with the shorter gallium–cobalt distance [Ga(1)]. In addition, this gallium atom Ga(1) has a weak isocarbonyl interaction ($d_{Ga–O}$ = 266.9 pm) with a CO of the [$Co(CO)_4$]$^–$ anion. Ga(2) is coordinated by a thf molecule with d_{GaO} = 220.6(5) pm, which is quite long for a Ga–O distance. For example, in thf adducts of gallium silyls, distances of between 201 and 210 pm are observed.[51] Clearly, the additional ligand at gallium has a slight influence on the gallium–cobalt bond and the gallium atom of LGa has become more Lewis acidic by coordination. The shorter gallium–nitrogen bonds compared with Ga(nacnac) and the short gallium–cobalt bond are a consequence of the use of the lone-pair for bonding, as discussed above.

Quantum Chemical Calculations

Digallane(4) [$R_2Ga_2\{Co(CO)_4\}_2$] [R = $Si(SiMe_3)_3$] was the expected product of the reaction in Equation (6). The model [$(Me_3Si)_2Ga_2\{Co(CO)_4\}_2$] (**13**; Figure 13) was studied by DFT methods [RI-DFT, BP86, def-SVC(P) using the Turbomole package].[66,67]

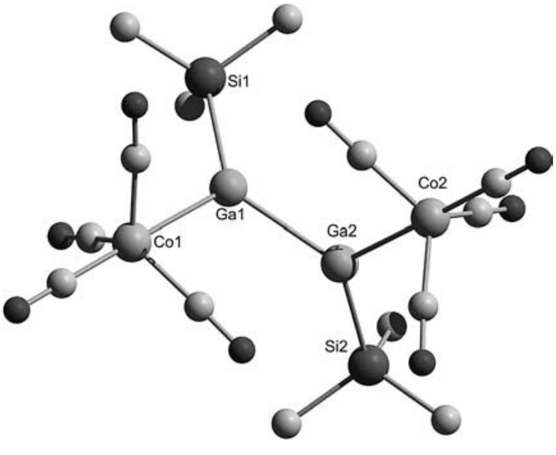


Figure 13. Molecular structure of **13** [BP86, def-SV(P)]. Hydrogen artoms have been omitted for clarity. Selected bond lengths [pm] and angles [°]: Ga(1)–Ga(2) 253.3, Co(1)–Ga(1) 248.3, Ga(1)–Si(1) 247.1, Co(1)–Ga(1)–Ga(2) 112.3, Co(1)–Ga(1)–Si(1) 119.5, Si(1)–Ga(1)–Ga(2) 128.0, Si(1)–Ga(1)–Ga(2)–Si(2) 90.6, Co(1)–Ga(1)–Ga(2)–Co(2) 100.6.

The Ga–Ga distance (d_{GaGa} = 253.3 pm) is comparable to that observed in bulky substituted digallane(4) derivatives. The Ga–Co distance ($d_{Ga–Co}$ = 248.3 pm) is shorter than observed for $[R_2Ga(donor)Co(CO)_4]$ complexes[61,68] and longer than in those with bridging RGa units. The CoSiGa planes are orthogonal to one another. This is typical of digallanes with bulky substituents. An Ahlrichs–Heinzmann[69–71] population analysis showed the Ga–Ga bond to be a typical single bond [shared electron number (SEN) 1.45]. The gallium atoms have a partial charge of 0.18, whereas cobalt atoms are negatively charged (–0.65).

The cation in **12** was optimized by DFT methods (Table 2). Most obvious is a shortening of the Ga–N bonds upon coordination to cobalt. This is explained by the use of the lone-pair of the gallium in Ga(nacnac), which is slightly Ga–N anti-bonding, for coordination. This is in line with an increase in the (SEN) for the Ga–N bonds and of the positive charge of the gallium atom.

Table 2. Selected bond lengths [pm] and angles [°] for [Co(CO)$_8$], Ga(nacnac) and **12** determined by RI-DFT calculations [BP86 functional, def-SV(P) basis set].

	$[Co_2(CO)_8]$	Ga(nacnac)	**12**
$d_{Ga–N}$ [pm]	–	212.1, 212.1	196.8, 196.6 197.0, 197.1
$d_{Co–Ga}$ [pm]	–	–	230.8, 230.3
α_{GaCoGa} [°]	–	–	176.0
SEN Ga–N	–	0.36	0.97
SEN Ga–Co	–	–	1.44
QGa (average)	–	0.35	0.45
QN (average)	–	–0.33	–0.11
QCo	–1.84	–	–1.94

Conclusion

The reactions of gallium subhalides with carbonylmetallates resulted in complexes with GaX (donor) ligands as well as in gallium–metal–oxo/hydroxo cages. The latter are caused by hydroxide impurities. Clearly, these organometallic groups are not valuable groups for the stabilization of gallium cluster compounds. Instead, redox disproportionation takes place to form gallium(III) complexes. The gallium–metal bond lengths are sensitive to the substituents on the four-coordinate gallium centres. Thus, iodine atoms bonded to the gallium atoms induce longer Ga–M bonds than chlorine or bromine atoms. Starting from the functional digallane $R_4Ga_4Cl_4$, the supramolecular arranged $[Ga\{Co_2(CO)_2\}_2]$ complex was obtained. Here, the counterion is responsible for the supramolecular arrangement. Cyclic hexamers are formed with the $[K(thf)]^+$ ion. These rings are connected to form channels. The small $[Li(thf)]^+$ cation only allows the formation of a dimer, whereas coordinationally nearly saturated $[K(toluene)_2]^+$ ions result in a linear polymer.[47,48] For the use of organometallic substituents in cluster stabilization, more bulky substituents like $Cp^*Fe(CO)_2$ might be useful.

Experimental Section

All procedures were performed under purified argon or in vacuo using Schlenk techniques. IR spectra were recorded by using KBr pellets with a Bruker IFS113v spectrometer. Elemental analyses were carried out in the microanalytical laboratory of the Institute of Inorganic Chemistry, University of Heidelberg. Mass spectra were recorded with a Varian MAT 711 spectrometer, and NMR spectra were recorded with a Bruker Advance II 400 spectrometer.

X-ray Crystallography: Suitable single crystals were mounted with perfluorinated polyether oil on the top of a glass fibre and cooled immediately on the goniometer head. Data collections were performed with graphite-monochromated Mo-K_α radiation with Stoe IPDS (**2–7**, **10–13**) and Bruker AXS (**1**, **8**, **9**) diffractometers using commercial software. Crystals of **8** were twinned. The *hkl* files were prepared by using GEMINI.[72] Structures were solved and refined by using the Bruker AXS SHELXTL software (PC) package.[73] All non-hydrogen atoms were refined anisotropically except for some carbon atoms of disordered thf molecules in **5**. All hydrogen atoms bonded to carbon atoms were placed geometrically and refined by using a riding model with fixed isotropic *U* values. Hydroxylic hydrogen atoms were taken from a difference Fourier map and refined isotropically (except for **11** in which oxygen-bonded H atoms could be detected; Tables 3, 4 and 5). CCDC-607654 (for **1**), -607655 (for **2**), -607656 (for **3**), -742709 (for **4**), -607657 (for **5**), -607658 (for **6**), -607659 (for **7**), -607660 (for **8**), -607661 (for **9**), -607662 (for **10**), -742710 (for **12**) and -733232 (for **13**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of $[(thf)GaClFe(CO)_4]_2$ (1): A solution of $Na_2[Fe(CO)_4]$ (0.43 g, 2.00 mmol)[74] in thf (20 mL) was added dropwise to a solution of Ga_2Cl_4·2dioxane (0.46 g, 1.00 mmol)[75] in thf (20 mL) with continuous stirring at –78 °C. The mixture was slowly warmed up to ambient temperature and stirred for an additional 2 h. The colour of the mixture turned red-brown and some grey precipitate formed at the end of the reaction. After the removal of all the volatiles in vacuo, the residue was redissolved in thf (20 mL). After filtration, yellow crystals were obtained by cooling the solution to –20 °C. Yield: 0.24 g of **1** (35% with respect to $Na_2[Fe(CO)_4]$). IR

Table 3. Crystal ctructure data for **1**–**4**.

	1	**2**	**3**	**4**
Empirical formula	$C_{16}H_{16}Cl_2Fe_2Ga_2O_{10}$	$C_{12}H_{16}Cl_2FeGaNaO_6$	$C_{24}H_{35}Cl_5Fe_2Ga_4O_{15}$	$C_{22}H_{32}Cl_4Fe_4Ga_8O_{15.50}$
Formula weight	690.33	475.71	1131.35	1467.44
Temperature [K]	190(2)	200(2)	200(2)	200(2)
Wavelength [pm]	71.073	71.073	71.073	71.073
Crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$P1$
Unit cell dimensions				
a [pm]	962.4(2)	958.17(19)	1081.7(2)	1217.8(2)
b [pm]	844.5(1)	1023.6(2)	1852.9(4)	1222.7(2)
c [pm]	1.505.6(3)	1122.7(2)	2039.7(4)	1477.3(3)
α [°]		64.68(3)		93.59(3)
β [°]	105.739(3)	69.71(3)	96.00(3)	90.23(3)
γ [°]		81.19(3)		109.86(3)
Volume [nm^3]	1.1778(3)	0.9336(3)	4.0660(14)	2.0639(7)
Z	2	2	4	2
Density (calculated) [g cm^{-3}]	1.947	1.692	1.848	2.361
Absorption coefficient [mm^{-1}]	3.745	2.550	3.695	6.807
$F(000)$	680	476	2240	1416
Crystal size [mm]	0.20 × 0.15 × 0.09	0.15 × 0.10 × 0.2	0.3 × 0.3 × 0.4	0.26 × 0.08 × 0.06
θ range for data collection [°]	2.27–32.42	3.15–25.89	2.19–25.87	1.38–20.80
Index ranges	$-13 \le h \le 13$, $0 \le k \le 12$, $0 \le l \le 22$	$-11 \le h \le 11$, $-12 \le k \le 12$, $-13 \le l \le 13$	$-13 \le h \le 13$, $-22 \le k \le 22$, $-24 \le l \le 24$	$-12 \le h \le 12$, $-12 \le k \le 12$, $-14 \le l \le 14$
Reflections collected	3948	8394	24668	8851
Independent reflections	3948 [R(int) = 0.0415]	3302 [R(int) = 0.0888]	7816 [R(int) = 0.0533]	7507 [R(int) = 0.1099]
Completeness to θ = 31.00° [%]	98.4	91.0	99.0	94.6
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	3948/0/177	3302/0/226	7816/0/479	7507/573/856
Goodness-of-fit on F^2	1.120	1.214	0.949	1.065
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0409$, $wR_2 = 0.1099$	$R_1 = 0.0423$, $wR_2 = 0.1166$	$R_1 = 0.0291$, $wR2 = 0.0635$	$R_1 = 0.095$, $wR2 = 0.215$
R indices (all data)	$R_1 = 0.0571$, $wR_2 = 0.1173$	$R_1 = 0.0505$, $wR_2 = 0.1335$	$R_1 = 0.0419$, $wR2 = 0.0666$	$R_1 = 0.1533$, $wR2 = 0.2362$
Largest diff. peak and hole [e Å^{-3}]	0.949 and –0.638	0.851 and –0.939	0.560 and –0.601	2.530 and –1.021
X-ray diffractometer	Bruker AXS	STOE IPDS	STOE IPDS	STOE IPDS

(KBr): $\tilde{\nu}_{CO}$ = 2089 (w), 2027 (s), 1996 (s), 1926 (m) cm^{-1}. $C_{16}H_{16}Cl_2Fe_2Ga_2O_{10}$ (690.2): calcd. C 27.84, H 2.32; found C 27.46, H 2.42.

Synthesis of {[(thf)$_2$Na(μ-Cl)$_2$GaFe(CO)$_4$]$_2$}$_n$ (2): A solution of $Na_2[Fe(CO)_4]$ (0.64 g, 3.00 mmol) in thf (20 mL) was added dropwise to a solution of Ga_2Cl_4·2dioxane (1.37 g, 3.00 mmol) in thf (20 mL) with continuous stirring at –78 °C. No change of colour was observed at –78 °C. The mixture was slowly warmed up to ambient temperature and stirred for another 4 h. The colour of the mixture turned brown and some grey precipitate formed at the end of the reaction. After the removal of all the volatiles in vacuo, the residue was redissolved in a mixture of diethyl ether and thf (5:1, 15 mL). Yellow crystals were obtained by over-laying the filtered mixture of diethyl ether and thf with pentane at ambient temperature. Yield: 0.46 g of **2** (38% based on iron). IR (KBr): $\tilde{\nu}_{CO}$ = 2026 (w), 2003 (s), 1972 (s), 1915 (m) cm^{-1}. MS [EI, 70 eV, M = $Na_2Cl_2Ga_2Fe_2(CO)_8$]: m/z (%) = 663.8 (0.3) [M]$^{+\cdot}$, 635.8 (0.4) [M – CO]$^{+\cdot}$, 607.7 (0.3) [M – 2CO]$^{+\cdot}$, 579.7 (1.6) [M – 3CO]$^{+\cdot}$, 551.6 (4.9) [M – 4CO]$^{+\cdot}$, 523.6 (6.3) [M – 5CO]$^{+\cdot}$, 495.6 (2.9) [M – 6CO]$^{+\cdot}$, 467.5 (1.9) [M – 7CO]$^{+\cdot}$, 439.5 (1.4) [M – 8CO]$^{+\cdot}$, 28.0 (100) [CO]$^{+\cdot}$. $C_8Cl_4Fe_2Ga_2Na_2O_8$·$2C_4H_8O$ (806.9): calcd. C 23.79, H 1.98; found C 23.99, H 2.15.

Synthesis of [(thf)Ga$_4$Cl$_5$(μ-OH)$_3${Fe(CO)$_4$}$_2$] (3): A solution of $Na_2[Fe(CO)_4]$ (0.78 g, 3.65 mmol) in thf (20 mL) was added dropwise to a solution of Ga_2Cl_4·2 dioxane (1.67 g, 3.65 mmol) in thf (20 mL) with continuous stirring at room temperature. The mixture was stirred for an additional 4 h at ambient temperature after addition. The colour of the mixture turned orange-red and some grey precipitate formed at the end of the reaction. After filtration through Celite and removal of all the volatiles in vacuo, the residue was redissolved in thf (15 mL). Colourless crystals were obtained by over-laying the solution of thf with pentane at ambient temperature. Yield: 0.18 g of **3** (22% based on iron). IR (KBr): $\tilde{\nu}_{CO}$ = 2085 (s), 2075 (s), 2045 (s), 2030 (s), 2004 (s), 1984 (s) cm^{-1}. MS [EI, 70 eV, M = $Ga_4Cl_5Fe_2(CO)_8(OH)_3$]: m/z (%) = 804.3 (1.0) [M – HCl – H]$^+$, 774.3 (1.5) [M – HCl – H – CO]$^+$, 746.3 (0.6) [M – HCl – H – 2CO]$^+$, 724.5 (3.3) [M – 3CO – Cl + 2H]$^+$, 718.3 (1.6) [M – HCl – H – 3CO]$^+$, 698.5 (6.9) [M – 3HCl – Cl]$^+$, 670.4 (6.3) [M – 5CO]$^{+\cdot}$, 495.6 (2.9) [M – 6CO]$^{+\cdot}$, 467.5 (1.9) [M – 7CO]$^{+\cdot}$, 439.5 (1.4) [M – 8CO]$^{+\cdot}$, 28.0 (100) [CO]$^{+\cdot}$. $C_{12}H_{11}Cl_5Fe_2Ga_4O_{12}$ (914.9): calcd. C 15.74, H 1.20; found C 15.63, H 1.14.

Synthesis of [Ga$_4$Cl$_4$(μ-OH)$_4${Fe(CO)$_4$}$_2$] (4): Ga_2Cl_4·2dioxane (1.08 g, 2.36 mmol) was dissolved in thf (10 mL) and $K_2[Fe(CO)_4]$ (1.15 g, 4.72 mmol) in thf (10 mL). Both solutions were added dropwise and simultaneously into thf (50 mL) at –78 °C with continuous stirring. The mixture was warmed to ambient temperature slowly and stirred for an additional 4 h. After removal of all the volatiles in vacuo, the residue was redissolved in toluene (15 mL). Colourless crystals were obtained at –30 °C. Yield: 0.20 g of **3** (17% based on gallium). IR (thf): $\tilde{\nu}_{CO}$ = 2020 (s), 1997 (vs) cm^{-1}.

Synthesis of [(thf)$_3$NaI(μ-I)Ga{Fe(CO)$_4$}]$_2$ (5): A solution of $Na_2[Fe(CO)_4]$[32] (0.64 g, 3.00 mmol) in thf (20 mL) was added dropwise to a suspension of "GaI" (1.37 g, 3.00 mmol) in thf

Table 4. Crystal structure data for **5**–**8**.

	5	**6**	**7**	**8**
Empirical formula	$C_{32}H_{48}Fe_2Ga_2I_4Na_2O_{14}$	$C_{84}H_{123}Fe_6Ga_6Na_5O_{46}$	$C_{13}H_{16}BrCrGaO_7$	$C_{36}H_{56}Cr_2GaI_3Na_2O_{15}$
Formula weight	1461.42	2737.19	485.89	1329.21
Temperature [K]	200(2)	200(2)	213(2)	190(2)
Wavelength [pm]	71.073	71.073	71.073	71.073
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P2_1/n$
Unit cell dimensions				
a [pm]	1041.0(2)	1995.6(2)	946.6(1)	1153.0(8)
b [pm]	1171.6(2)	2419.3(2)	1324.2(2)	2124.6(1)
c [pm]	1196.0(2)	2579.3(2)	1590.9(3)	2118.7(9)
α [°]	70.77(3)		112.75(2)	
β [°]	68.57(3)	97.29(1)	94.90(2)	98.81(3)
γ [°]	84.02(3)		90.23(2)	
Volume [nm^3]	1.2818(4)	12.3521(19)	1.8308(5)	5.129(5)
Z	1	4	4	4
Density (calculated) [g cm^{-3}]	1.893	1.475	1.763	1.721
Absorption coefficient [mm^{-1}]	4.071	2.062	4.275	2.817
F(000)	700	5588	960	2608
Crystal size [mm]	0.3 × 0.2 × 0.1	0.35 × 0.4 × 0.5	0.5 × 0.4 × 0.2	0.48 × 0.18 × 0.18
θ range for data collection [°]	2.56–26.08	1.97–25.80	2.16–28.00	1.90–25.00
Index ranges	$-12 \le h \le 12$, $-13 \le k \le 13$, $-14 \le l \le 14$	$-24 \le h \le 23$, $-29 \le k \le 29$, $-31 \le l \le 31$	$-12 \le h \le 12$ $-17 \le k \le 17$ $-20 \le l \le 20$	$-10 \le h \le 10$ $-25 \le k \le 25$ $-24 \le l \le 24$
Reflections collected	9906	68794	19520	40485
Independent reflections	4630 [R(int) = 0.0644]	22385 [R(int) = 0.1999]	8145 [R(int) = 0.0850]	40488 [R(int) = 0.0000]
Completeness to θ = 31.00° [%]	91.2	94.1	92.0	70.9
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	4630/0/193	22385/2530/1696	8145/0/415	40488/0/556
Goodness-of-fit on F^2	1.029	0.973	0.757	1.004
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0443$, $wR_2 = 0.1283$	$R_1 = 0.0788$, $wR_2 = 0.1779$	$R_1 = 0.0372$, $wR_2 = 0.0722$	$R_1 = 0.0795$, $wR_2 = 0.2053$
R indices (all data)	$R_1 = 0.0585$, $wR_2 = 0.1362$	$R_1 = 0.1358$, $wR_2 = 0.2152$	$R_1 = 0.0829$, $wR_2 = 0.0827$	$R_1 = 0.1293$, $wR_2 = 0.2504$
Largest diff. peak and hole [e Å^{-3}]	0.946 and –0.846	1.061 and –0.888	0.776 and –0.504	1.844 and –2.119
X-ray diffractometer	STOE IPDS	STOE IPDS	STOE IPDS	Bruker AXS

(20 mL) with continuous stirring at –78 °C. No change of colour was observed at –78 °C. The mixture was slowly warmed up to ambient temperature and stirred for another 4 h. The colour of the mixture turned brown and some grey precipitate formed at the end of the reaction. After the removal of all the volatiles in vacuo, the residue was redissolved in a mixture of diethyl ether and thf (5:1, 15 mL). Yellow crystals were obtained by over-laying the mixture of diethyl ether and thf with pentane at ambient temperature. Yield: 0.49 g of **5** (25% based on iron). IR (KBr): $\tilde{\nu}_{CO}$ = 2033 (s), 2006 (s), 1974 (s), 1880 (s) cm^{-1}. MS [EI, 70 eV, M = $Na_2I_2Ga_2Fe_2(CO)_8$]: m/z (%) = 1001.9 (0.1) [M – CO]$^{+\cdot}$, 973.8 (0.2) [M – 2CO]$^{+\cdot}$, 945.7 (0.2) [M – 3CO]$^{+\cdot}$, 889.8 (0.2) [M – 5CO]$^{+\cdot}$, 861.7 (0.1) [M – 6CO]$^{+\cdot}$, 833.5 (0.3) [M – 7CO]$^{+\cdot}$, 805.1 (0.6) [M – 8CO]$^{+\cdot}$, 449.5 (100) [GaI_3]$^{+\cdot}$, 322.6 (79.5) [GaI_2]$^{+}$. $C_8Fe_2Ga_2I_4Na_2O_8\cdot 4C_4H_8O$ (1316.8): calcd. C 21.87, H 2.43; found C 21.33, H 2.19.

Synthesis of [$Na_5(thf)_{14}\{GaFe(CO)_4\}_6(\mu^3\text{-}O)_4(\mu\text{-}OH)_3$] (6): A suspension of "GaI" (4.00 mmol) in toluene (20 mL) was added dropwise to a suspension of $Na_2[Fe(CO)_4]$ (0.43 g, 2.00 mmol) in toluene (20 mL) with continuous stirring at –78 °C. No change of colour was observed at –78 °C. The mixture was slowly warmed up to ambient temperature and stirred for another 10 h at room temperature. The colour of the mixture turned brown and some grey precipitate formed at the end of the reaction. After the removal of all the volatiles in vacuo, the residue was redissolved in thf (15 mL). Colourless crystals were obtained by over-laying the solution of thf with pentane at ambient temperature. Yield: 0.12 g of **5** (18% based on iron). IR (KBr): $\tilde{\nu}_{CO}$ = 2008 (s), 1869 (s) cm^{-1}. $C_{24}H_3Fe_6Ga_6Na_5O_{31}\cdot 5C_4H_8O$ (2015.4): calcd. C 26.19, H 2.13; found C 25.43, H 2.14.

Synthesis of [$(thf)_2GaBrCr(CO)_5$] (7): A solution of $Na_2[Cr(CO)_5]$ (0.31 g, 1.30 mmol)[76] in thf (20 mL) was added dropwise to a solution of $Ga_2Br_4\cdot 2dioxane$ (0.56 g, 0.85 mmol)[75] in thf (20 mL) with continuous stirring at –78 °C. After addition, the mixture was slowly warmed up to ambient temperature and stirred for an additional 2 h. The colour of the suspension turned grey-brown at the end of the reaction. After the removal of all the volatiles in vacuo, the residue was extracted consecutively in diethyl ether (15 mL) and thf (15 mL). Colourless crystals were obtained by over-laying the solution of thf with pentane at –20 °C. Yield: 0.59 g of **7** (35% with respect to Cr). IR (KBr): $\tilde{\nu}_{CO}$ = 2061 (m), 1989 (s), 1911 (vs) cm^{-1}. MS [EI, 70 eV, M = $BrGaCr(CO)_5$]: m/z (%) = 342 (85) [M]$^{+\cdot}$, 314 (39) [M – CO]$^{+\cdot}$, 258 (3) [M – 3CO]$^{+\cdot}$, 230 (5) [M – 4CO]$^{+\cdot}$, 202 (15) [M – 5CO]$^{+\cdot}$, 72 (100) [thf]$^{+\cdot}$. $C_{13}H_{16}BrCrGaO_7$ (485.7): calcd. C 32.12, H 3.29; found C 31.60, H 3.25.

Synthesis of [$(thf)_7Na_2GaI(\mu\text{-}I)_2\{Cr(CO)_4\}_2$]$_n$ (8): A suspension of "GaI" (2.23 mmol) in toluene (20 mL) was added dropwise to a solution of $Na_2[Cr(CO)_5]$ (0.27 g, 1.13 mmol) in toluene (20 mL) with continuous stirring at –78 °C. After addition, the mixture was slowly warmed up to ambient temperature and stirred for an additional 3 h. The colour of the suspension turned yellow-brown at the end of the reaction. After the removal of toluene solution by filtration, the residue was redissolved in diethyl ether (15 mL). Red crystals were obtained by laying the solution of diethyl ether over pentane at –20 °C. Yield: 0.32 g of **8** (42% with respect to Cr). IR

Table 5. Crystal structure data for **11** and **12**.

	11	**12**
Empirical formula	$C_{19}H_9Co_4GaKO_{15}$	$C_{77}H_{106}Co_2Ga_2N_4O_{10}$
*F*ormula weight	821.80	1504.96
Temperature [K]	200(2)	200(2)
Wavelength [pm]	71.073	71.073
Crystal system	Hexagonal	Triclinic
Space group	$R\bar{3}$	$P\bar{1}$
Unit cell dimensions		
a [pm]	3699.0(5)	1293.5(3)
b [pm]		1474.2(3)
c [pm]	1067.7(2)	2246.0(5)
α [°]		84.05(3)
β [°]		75.18(3)
γ [°]		68.19(3)
Volume [nm^3]	12.651(4)	3.844(1)
Z	18	2
Density (calculated) [$g\,cm^{-3}$]	1.942	1.300
Absorption coefficient [mm^{-1}]	3.472	1.175
F(000)	7218	1584
Crystal size [mm]	0.60 × 0.05 × 0.04	0.35 × 0.18 × 0.37
θ range for data collection [°]	2.2–28.2	1.5–21.0
Index ranges	$-48 \le h \le 48$ $-48 \le k \le 49$ $-14 \le l \le 14$	$-12 \le h \le 12$ $-14 \le k \le 14$ $-22 \le l \le 22$
Reflections collected	41622	17011
Independent reflections	6872 [*R*(int) = 0.099]	7815[*R*(int) = 0.0948]
Completeness to θ = 31.00° [%]	99.2	95.1
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	6872/0/356	7815/0/876
Goodness-of-fit on F^2	0.839	0.847
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0384$, $wR_2 = 0.0875$	$R_1 = 0.065$; $wR_2 = 0.145$
R indices (all data)	$R_1 = 0.0817$, $wR_2 = 0.0983$	$R_1 = 0.124$; $wR_2 = 0.161$
Largest diff. peak and hole [$e\,Å^{-3}$]	2.020 and –0.472	1.05 and –0.74
X-ray diffractometer	STOE IPDS I	STOE IPDS I

(KBr): $\tilde{\nu}_{CO}$ = 2057 (w), 1938 (s), 1869 (s), 1645 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 254 (100) $[I_2]^{+\cdot}$, 127 (18) $[I]^+$, 72 (66) $[thf]^{+\cdot}$. $C_{36}H_{56}Cr_2GaI_3Na_2O_{15}$ (1328.4): calcd. C 32.52, H 4.22; found C 31.98, H 3.89.

Synthesis of $[(thf)_4Na_2(\mu^4\text{-}OH)(\mu^3\text{-}OH)_2GaCr(CO)_5]_2$ (9): A suspension of "GaI" (2.00 mmol) in toluene (20 mL) was added dropwise to a solution of $Na_2[Cr(CO)_5]$ (0.47 g, 2.00 mmol) in thf (20 mL) with continuous stirring at –78 °C. The mixture was slowly warmed up to ambient temperature and stirred for another 4 h. No change of colour was observed at the end of the reaction. After filtration, all volatiles in toluene solution were removed in vacuo. The residue was redissolved in a mixture of diethyl ether and thf (1:1, 15 mL). Colourless crystals were obtained by over-laying the mixture of diethyl ether and thf with pentane at ambient temperature. Yield: 0.29 g of **9** (23% with respect to Cr). IR (KBr): $\tilde{\nu}_{CO}$ = 2020 (w), 1972 (s), 1945 (m) cm^{-1}. $C_{42}H_{70}Cr_2Ga_2\ Na_4O_{24}$ (1293.4): calcd. C 38.97, H 5.46; found C 38.80, H 5.08.

Synthesis of $[Na(thf)_6]_2[Na_3(thf)_{10}\{(CO)_5CrGa\}_6(\mu_3\text{-}O)_3(\mu_3\text{-}OH)_5]$-$[Na_3(thf)_{10}\{(CO)_5CrGa\}_6(\mu^3\text{-}O)_2(\mu\text{-}OH)_5]_n$ (10): A suspension of "GaI" (3.28 mmol) in toluene (20 mL) was added dropwise to a solution of $Na_2[Cr(CO)_5]$ (0.39 g, 1.64 mmol) in toluene (20 mL) with continuous stirring at –78 °C. No change of colour was observed at –78 °C after the addition. The mixture was slowly warmed up to ambient temperature and stirred for another 12 h at room temperature. The colour of the mixture turned pale yellow and some grey precipitate formed at the end of the reaction. After the removal of all the volatiles in vacuo, the residue was redissolved in thf (15 mL). Colourless and yellow crystals were obtained by overlaying the solution of thf with pentane at ambient temperature. Yield: 0.25 g of **10** (40% with respect to Cr). IR (KBr): $\tilde{\nu}_{CO}$ = 1850 (s), 1816 (s) cm^{-1}. $C_{60}H_{10}Cr_{12}Ga_{12}Na_8O_{75}\cdot16C_4H_8O$ (4726.4): calcd. C 31.48, H 2.92; found C 31.21, H 2.46.

Synthesis of 11: A solution of $K[Co(CO)_4]$ (0.87 g, 4.1 mmol) in thf (5 mL) was added dropwise into a solution of $Ga_4Cl_4\{Si(SiMe_3)_3\}_4$ (1.36 g, 1.0 mmol) in thf (10 mL) at –78 °C. After warming to ambient temperatures and stirring overnight all the volatiles were removed in vacuo. The brown residue was washed with hexane and toluene and then dissolved in thf. At ambient temperature several yellow needles of **11** were deposited. Crystals suitable for X-ray crystal structure determination were obtained from a $[D_6]$benzene solution. IR (KBr): $\tilde{\nu}_{CO}$ = 1968 (s), 1764 (m) cm^{-1}.

Synthesis of 12: A solution of Ga(nacnac) (1.74 g, 3.5 mmol) in toluene (20 mL) was cooled to –40 °C. $[Co_2(CO)_8]$ (0.61 g, 1.78 mmol) was added with stirring. The reaction mixture was warmed to ambient temperature and stirred for 1 h. During this time a precipitate formed, which was separated by centrifugation. The residue was dissolved in thf and the solution was cooled to –30 °C. Yellow crystals of **12** were obtained. Yield: 0.21 g (15%). ^1H NMR (C_6D_6): δ = 7.17 (m, 12 H, CH arom.), 5.49 (s, 2 H, CH), 2.94 (m, 8 H, C*H*Me$_2$), 1.68 (s 12 H, CMe), 1.12 (d, 24 H, CH*Me*$_2$), 1.11 (d, 24 H, CH*Me*$_2$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 196.3 (CO), 170.8 (CO), 161.3 [N-*C*(dipp)], 143.1 (*C*Me), 142.5 [*o*-*C*(dipp)], 125.4 [*p*-*C*(dipp)], 124.6 [*m*-*C*(dipp)], 102.7 (CH), 28.8 (*C*HMe$_2$), 24.4 (CH*Me*$_2$), 24.1 (C*Me*), 23.2 (CH*Me*$_2$) ppm. IR (C_6D_6): $\tilde{\nu}$ = 1941 (s, CO), 1857 (s, CO), 1802 (s), 1736 (w), 1490 (s), 1379 (s), 1178 (s), 1041 (s) cm^{-1}.

Supporting Information (see footnote on the first page of this article): Information on crystal structure analyses of **9** and **10**.

Acknowledgments

We thank Philipp Butzug for assisting in the collection of the X-ray data. Financial support by the Deutsche Forschungsgemeinschaft (DFG) is gratefully acknowledged.

---

[1] R. A. Fischer, J. Weiß, *Angew. Chem.* **1999**, *113*, 589–591; *Angew. Chem. Int. Ed.* **1999**, *38*, 2830–2850.
[2] G. Linti, H. Schnöckel, *Coord. Chem. Rev.* **2000**, *206–207*, 285–319.
[3] N. A. Compton, R. J. Errington, N. C. Norman, *Adv. Organomet. Chem.* **1990**, *31*, 91–182.
[4] P. Corradini, A. Sirigu, *Inorg. Chem.* **1967**, *6*, 601–605.
[5] H.-J. Himmel, G. Linti, *Angew. Chem.* **2008**, *120*, 6425–6427; *Angew. Chem. Int. Ed.* **2008**, *47*, 6326–6328.
[6] C. Gemel, T. Steinke, M. Cokoja, A. Kampter, R. A. Fischer, *Eur. J. Inorg. Chem.* **2004**, 4161–4176.
[7] R. J. Baker, C. Jones, *Coord. Chem. Rev.* **2005**, *249*, 1857–1869.
[8] P. Jutzi, B. Neumann, G. Reumann, H.-G. Stammler, *Organometallics* **1998**, *17*, 1305–1314.
[9] G. Linti, W. Köstler, *Chem. Eur. J.* **1998**, *4*, 942–949.
[10] W. Uhl, M. Benter, S. Melle, W. Saak, G. Frenking, J. Uddin, *Organometallics* **1999**, *18*, 3778–3780.
[11] W. Uhl, M. Pohlmann, R. Wartchow, *Angew. Chem.* **1998**, *110*, 1007–1009; *Angew. Chem. Int. Ed.* **1998**, *37*, 961–963.
[12] G. Linti, A. Seifert, *Inorg. Chem.* **2008**, *47*, 11398–11404.
[13] C. Böhme, G. Frenking, *Chem. Eur. J.* **1999**, *5*, 2184–2190.
[14] G. Frenking, *J. Organomet. Chem.* **2001**, *635*, 9–23.
[15] F. A. Cotton, X. Feng, *Organometallics* **1998**, *17*, 128–130.
[16] R. Köppe, H. Schnöckel, *Z. Anorg. Allg. Chem.* **2000**, *626*, 1095–1099.
[17] J. Su, X.-W. Li, R. C. Crittendon, C. F. Campana, G. H. Robinson, *Organometallics* **1997**, *16*, 4511–4513.
[18] N. D. Coombs, W. Clegg, A. L. Thompson, D. J. Willock, S. Aldridge, *J. Am. Chem. Soc.* **2008**, *130*, 5449–5451.
[19] T. Cadenbach, C. Gemel, D. Zacher, R. A. Fischer, *Angew. Chem.* **2008**, *120*, 3487–3490; *Angew. Chem. Int. Ed.* **2008**, *47*, 3438–3441.
[20] B. Buchin, C. Gemel, T. Cadenbach, I. Fernandes, G. Frenking, R. A. Fischer, *Angew. Chem.* **2006**, *118*, 5331–5334; *Angew. Chem. Int. Ed.* **2006**, *45*, 5207–5210.
[21] P. Jutzi, B. Neumann, G. Reumann, L. O. Schebaum, A. Stammler, *Organometallics* **1999**, *18*, 4462–4464.
[22] T. Steinke, C. Gemal, M. Winter, R. A. Fischer, *Chem. Eur. J.* **2005**, *11*, 1636–1646.
[23] B. Buchin, C. Gemel, T. Cadenbach, R. A. Fischer, *Inorg. Chem.* **2006**, *45*, 1789–1794.
[24] N. J. Hardman, P. P. Power, J. D. Gordon, C. L. B. Macdonald, A. H. Cowley, *Chem. Commun.* **2001**, 1866–1867.
[25] R. J. Baker, C. Jones, *Dalton Trans.* **2005**, 1341–1348.
[26] R. J. Baker, C. Jones, D. M. Murphy, *Chem. Commun.* **2005**, 1339–1341.
[27] G. Linti, H. Schnöckel, W. Uhl, N. Wiberg in *Molecular Clusters of the Main Group Elements* (Eds.: M. Driess, H. Nöth), Wiley-VCH, Weinheim, **2004**, pp. 126–168.
[28] H. Schnöckel, A. Schnepf, *Angew. Chem.* **2002**, *114*, 3683–3704; *Angew. Chem. Int. Ed.* **2002**, *41*, 3532–3552.
[29] H. Schnöckel, *Dalton Trans.* **2008**, 4344–4362.
[30] H. Schnöckel, A. Schnepf in *The Group 13 Metals* (Eds.: S. Aldridge, A. J. Downs), Wiley, Chichester, **2011**.
[31] N. R. Burns, S. Aldridge, D. L. Coombs, A. Rossini, D. J. Willcock, C. Jones, L. Ooi, *Chem. Commun.* **2004**, 1732–1733.
[32] M. L. H. Green, P. Mountford, G. J. Smout, S. R. Speel, *Polyhedron* **1990**, *9*, 2763–2765.
[33] G. Linti, W. Köstler, *Angew. Chem.* **1996**, *108*, 593–595; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 550–552.
[34] R. C. Crittendon, X.-W. Li, J. Su, G. H. Robinson, *Organometallics* **1997**, *16*, 2443–2447.
[35] U. App, K. Merzweiler, *Z. Anorg. Allg. Chem.* **1997**, *623*, 478–482.
[36] R. A. Fischer, A. Miehr, T. Priermeier, *Chem. Ber.* **1995**, *128*, 831–843.
[37] G. Linti, G. Li, *J. Organomet. Chem.* **2001**, *626*, 82–91.
[38] R. A. Fischer, T. Priermeier, W. Scherer, *J. Organomet. Chem.* **1993**, *459*, 65–71.
[39] W. Uhl, A. El-Hamdan, W. Petz, G. Geiseler, K. Harms, *Z. Naturforsch., B* **2004**, *59*, 789–792.
[40] X. He, R. A. Bartlett, P. P. Power, *Organometallics* **1994**, *13*, 548–552.
[41] R. A. Fischer, M. M. Schulte, E. Herdtweck, M. R. Mattner, *Inorg. Chem.* **1997**, *36*, 2010–2017.
[42] R. M. Campbell, L. M. Clarkson, W. Clegg, D. C. R. Hockless, N. L. Pickett, N. C. Norman, *Chem. Ber.* **1992**, *125*, 55–59.
[43] J. C. Vanderhooft, R. D. Ernst, F. W. Cagle, R. J. Neustadt, T. H. Cymbaluk, *Inorg. Chem.* **1982**, *21*, 1876–1880.
[44] A. Schnepf, G. Stößer, D. Carmichael, F. Mathey, H. Schnöckel, *Angew. Chem.* **1999**, *111*, 1757–1759; *Angew. Chem. Int. Ed.* **1999**, *38*, 1646–1649.
[45] R. A. Fischer, M. M. Schulte, J. Weiss, L. Z. Zolnai, A. Jacobi, G. Huttner, G. Frenking, C. Boehm, S. F. Vyboishchikov, *J. Am. Chem. Soc.* **1998**, *120*, 1237–1248.
[46] M. M. Schulte, E. Herdweck, C. Raudaschl-Sieber, R. A. Fischer, *Angew. Chem.* **1996**, *108*, 489–491; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 424–427.
[47] E. Leiner, M. Scheer, *J. Org. Chem.* **2002**, *646*, 247–254.
[48] E. Leiner, O. Hampe, M. Scheer, *Eur. J. Inorg. Chem.* **2002**, 584–590.
[49] A. Seifert, D. Scheid, G. Linti, T. Zessin, *Chem. Eur. J.* **2009**, *15*, 12114–12120.
[50] A. Kempter, C. Gemel, R. A. Fischer, *Inorg. Chem.* **2008**, *47*, 7279–7285.
[51] G. Linti, R. Frey, W. Köstler, H. Urban, *Chem. Ber.* **1996**, *129*, 561–569.
[52] A. R. Barron, K. D. Dobbs, M. M. Franci, *J. Am. Chem. Soc.* **1991**, *113*, 39–43.
[53] A. R. Barron, *Chem. Soc. Rev.* **1993**, *22*, 93–99.
[54] C. Schnitter, H. W. Roesky, T. Albers, H.-G. Schmidt, C. Röpken, E. Parisini, G. M. Sheldrick, *Chem. Eur. J.* **1997**, *3*, 1783–1792.
[55] N. Wiberg, T. Blank, K. Amelunxen, H. Nöth, H. Schnöckel, E. Baum, A. Purath, D. Tenske, *Eur. J. Inorg. Chem.* **2002**, 341–350.
[56] J. Storre, T. Belgardt, D. Stalke, H. W. Roesky, *Angew. Chem.* **1994**, *106*, 1365–1366; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1244–1246.
[57] B. Neumüller, F. Gahlmann, *Angew. Chem.* **1993**, *105*, 1770–1771; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1701–1702.
[58] J. Storre, A. Klump, H. W. Roesky, R. Fleischer, D. Stalke, *Organometallics* **1997**, *16*, 3074–3076.
[59] C. J. Harlan, S. G. Bott, A. R. Barron, *J. Am. Chem. Soc.* **1995**, *117*, 6465–6474.
[60] A. S. Borovik, S. G. Bott, A. R. Barron, *Organometallics* **1999**, *18*, 2668–2676.
[61] R. A. Fischer, A. Miehr, H. Hoffmann, W. Rogge, C. Boehme, G. Frenking, E. Herdweck, *Z. Anorg. Allg. Chem.* **1999**, *625*, 1466–1474.
[62] R. A. Fischer, C. Boehme, *Chem. Ber.* **1992**, *125*, 37–42.
[63] A. Kempter, C. Gemel, R. A. Fischer, *Chem. Eur. J.* **2007**, *13*, 2990–3000.
[64] N. J. Hardman, R. J. Wright, A. D. Phillips, P. P. Power, *J. Am. Chem. Soc.* **2003**, *125*, 2667–2679.
[65] A. Kempter, C. Gemel, R. A. Fischer, *Inorg. Chem.* **2005**, *44*, 163–165.
[66] K. Eichkorn, O. Treutler, H. Oehm, M. Haeser, R. Ahlrichs, *Chem. Phys. Lett.* **1995**, *242*, 652–660.
[67] O. Treutler, R. Ahlrichs, *J. Chem. Phys.* **1995**, *102*, 346–354.

[68] T. Clark, C. A. Jaska, A. Turak, A. J. Lough, Z. H. Lu, I. Manners, *Inorg. Chem.* **2007**, *46*, 7394–7402.
[69] R. Heinzmann, R. Ahlrichs, *Theor. Chim. Acta* **1976**, *42*, 33–45.
[70] K. R. Roby, *Mol. Phys.* **1974**, *27*, 81–104.
[71] E. R. Davidson, *J. Chem. Phys.* **1967**, *46*, 3320–3324.
[72] E. Stanley, *J. Appl. Crystallogr.* **1972**, *5*, 191–194.
[73] G. M. Sheldrick, *SHELXTL* 5.1, Bruker AXS, Madison, **1998**; G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122.
[74] H. Strong, P. J. Krusie, J. SanFilippo Jr., *Inorg. Synth.* **1990**, *28*, 203–207.
[75] J. C. Beamish, M. W. Wilkinson, I. J. Worrath, *Inorg. Chem.* **1978**, *17*, 2026–2027.
[76] M. A. Schwindt, P. Lejon, L. S. Hegedus, *Organometallics* **1990**, *9*, 2814–2819.

Received: March 21, 2011