

Replacement of CO ligands by the isolobal gallium(I) compound GaR [R = C(SiMe₃)₃], formation of the transition metal gallium compounds Mn₂(CO)₈(μ-GaR)₂ and Fe₃(CO)₉(μ-CO)(μ-GaR)₂

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The tetrahedral alkylgallium(I) compound Ga₄R₄ **1** [R = C(SiMe₃)₃] dissociates in solution with the formation of the monomeric fragments GaR, which are isolobal to carbon monoxide and are able to replace CO ligands in transition metal carbonyl complexes. By the substitution of two CO groups, the treatment of Mn₂(CO)₁₀ and Fe₃(CO)₁₂ with **1** yielded the two novel transition metal gallium complexes Mn₂(CO)₈(μ-GaR)₂ **2** and Fe₃(CO)₉(μ-CO)(μ-GaR)₂ **3**, neither of which is isostructural to the starting carbonyl compounds. The GaR ligands bridge both manganese atoms of **2** with all carbonyl groups in terminal positions, and two edges of the central Fe₃ triangle of **3** are occupied by GaR, while the third one is bridged by carbon monoxide.

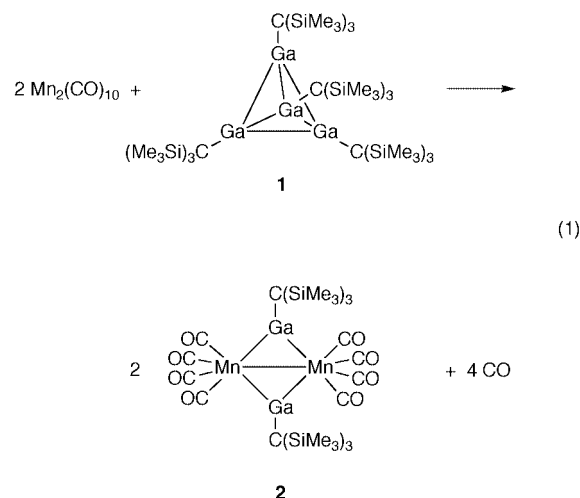
In the past, we have published facile methods for the syntheses of the alkylgallium(I) compounds Ga₄[C(SiMe₃)₃]₄ (**1**)¹ and In₄[C(SiMe₃)₃]₄,² both of which have almost undistorted tetrahedra of four gallium or indium atoms in the solid state. The gallium compound dissociates upon dissolution in benzene to yield the monomeric fragment GaR, which was also detected in the gas phase and characterized by an electron diffraction experiment.³ In contrast, the indium analogue remains a tetramer in solution, and monomeric alkylindium(I) derivatives were only observed by employing very large substituents such as C(SiMe₂iPr)₃.⁴ These monomers have a lone electron pair and two empty p-orbitals perpendicular to the E–C bond axis and thus have frontier orbitals similar to those of carbon monoxide. Indeed, we succeeded in synthesizing many transition metal indium complexes, when we treated dinuclear carbonyl compounds with the tetraindium derivative.^{5–7} But in most cases, the InR groups occupied bridging positions across M–M bonds. A terminal co-ordination of the InR ligand was observed for the compound Ni[InC(SiMe₃)₃]₄,⁸ which is a remarkable analogue of tetracarbonylnickel. Its central nickel atom is tetrahedrally co-ordinated by four indium atoms with very short Ni–In bond lengths. The analogous gallium compound was obtained only recently,⁹ and quantum chemical calculations verified a very effective π-back bonding of electron density from the nickel to the gallium or indium atoms.⁹ The NiGa₄ derivative is the only co-ordination compound bearing the alkylgallium(I) ligand Ga–C(SiMe₃)₃ obtained so far, and, in contrast to the facile syntheses of the corresponding transition metal indium compounds, the analogous reactions of **1** proved to be very difficult yielding complicated mixtures of products in many cases. We wish to report here on the first successful reactions of **1** with decacarbonyldimanganese and nonacarbonyltriiron. In contrast to alkylgallium(I), the cyclopentadienyl derivative GaCp*¹⁰ with a pentahapto co-ordinated pentamethylcyclopentadienyl group has been used several times before for the synthesis of transition metal complexes and clusters.¹¹ The synthesis of aluminium, gallium and indium co-ordination compounds on different routes and their application to the deposition of alloys was described only recently.¹²

Results

Synthesis and crystal structure of Mn₂(CO)₈(μ-GaR)₂ **2**

Reaction of the red tetragallium compound **1** with decacarbon-

ylmanganese in toluene at 60 °C afforded an orange solution of a mixture of several compounds, which gave five singlets of SiMe₃ groups with different intensities in the ¹H NMR spectrum. Only one compound (**2**) could be isolated in a pure form by recrystallization in a low yield of only 17%. All attempts to obtain a further product by recrystallization from different solvents or by sublimation failed. Owing to the results of the elemental analysis of **2**, two CO groups of the starting carbonyl complex have been replaced by GaR ligands, eqn. (1). Compound **2** showed a singlet of the tri-



methylsilyl groups in the ¹H and ¹³C NMR spectra. The resonance of the α carbon atom of the trisilylmethyl group was detected at δ 48.8, it was considerably shifted to a higher field compared to that of the gallium(I) compound **1** (δ 62¹). Similar shifts compared to the alkylindium(I) starting compound were observed for analogous InR complexes.^{5–7} Carbon atoms attached to the trivalent elements gallium and indium in tri-alkyl derivatives are usually observed below δ 30. Thus, the unusual chemical shifts detected for the transition metal gallium or indium compounds may be caused by the particular bonding situation in these complexes. The carbonyl groups of **2** gave a single resonance at δ 218.2 at room temperature. However, owing to the particular molecular structure of **2** with two bridging GaR ligands two different CO resonances should

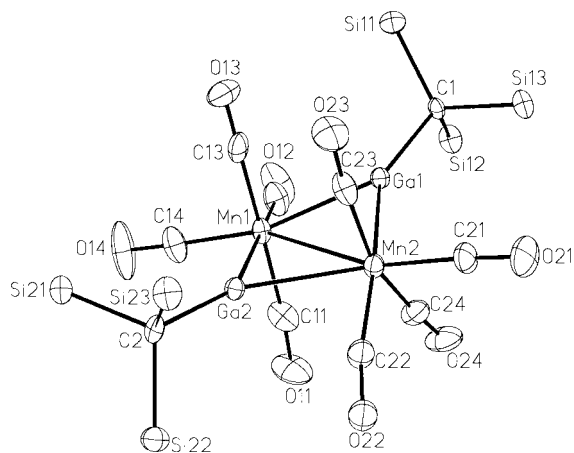


Fig. 1 Molecular structure and numbering scheme of compound **2**; the thermal ellipsoids are drawn at the 40% probability level; methyl groups are omitted for clarity.

result, one for those CO groups which are in plane with the Ga atoms and one for the axially co-ordinated CO ligands. The fast equilibration process could not be frozen even upon cooling of a solution in toluene to 213 K. Only the absorptions of terminally co-ordinated CO groups were detected in the IR spectrum between 2044 and 1920 cm^{-1} .

The molecular structure of **2** (Fig. 1) is similar to that of the indium analogue,⁶ although the compounds are not isotopic. Both manganese atoms are bridged by two GaR groups, and each manganese atom is further co-ordinated by four terminal CO ligands, of which two are in plane with the Mn and Ga atoms. The Mn–Mn distance (295.0 pm, Table 1) is only slightly longer than that of $\text{Mn}_2(\text{CO})_{10}$ (292 pm),¹³ but considerably shortened compared to that of the InR bridged derivative (313.7 pm). The separation of the transition metal atoms in such dinuclear complexes seems to be determined by the covalent radius of the bridging atoms, and the long Mn–In bond lengths (263 pm on average) in $\text{Mn}_2(\text{CO})_8\text{In}_2\{\text{C}(\text{SiMe}_3)_3\}_2$ appear to force the Mn atoms further apart than in $\text{Mn}_2(\text{CO})_{10}$. The GaR bridges are unsymmetric, and different Mn–Ga distances of 242.7 and 256.1 pm on average are observed at each Mn atom. A kind of semi-bridging situation results, with the Ga–C bond axes almost ideally perpendicular to the Mn1–Mn2 axis (Ga1–C1 89.7°; Ga2–C2 88.0°). The Mn–Ga bond lengths are within the range usually observed.¹⁴ In contrast to the Mn_2In_2 derivative⁶ the Mn_2Ga_2 molecular core of **2** is not planar, but folded across the Mn–Mn axis by 21.9°.

Synthesis and crystal structure of $\text{Fe}_3(\text{CO})_9(\mu\text{-CO})(\mu\text{-GaR})_2$ **3**

As reported earlier, the tetraindium analogue of **1** reacted with $\text{Fe}_3(\text{CO})_{12}$ by replacement of two CO ligands by InR groups.⁶ A compound was formed which was isostructural to the starting carbonyl complex and had both InR groups in a bridging position above one edge of the Fe_3 triangle, while two Fe–Fe bonds remained unsupported (Chart 1). In a similar reaction, a mixture of $\text{Fe}_3(\text{CO})_{12}$ and the tetragallium compound **1** in a molar ratio of 2 to 1 was heated in *n*-hexane under reflux for 3 hours, eqn. (2). Compound **1** was completely consumed, and a deep

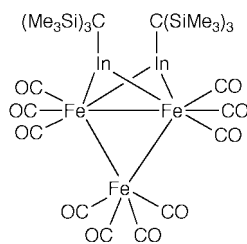
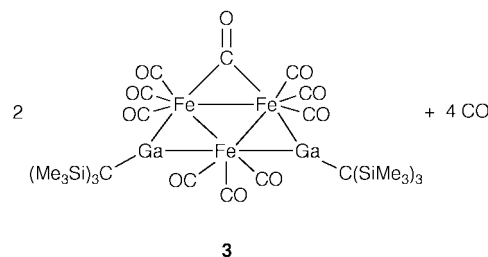
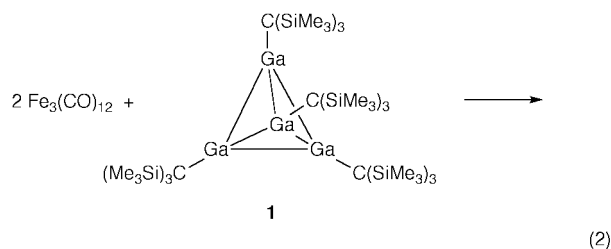


Chart 1

Table 1 Selected bond lengths (pm) and angles (°)

Compound 2			
Ga1–Mn1	253.0(2)	Ga2–Mn1	242.4(1)
Ga1–Mn2	243.0(2)	Ga2–Mn2	259.1(2)
Ga1–C1	198.7(7)	Ga2–C2	199.9(7)
Mn1–Mn2	295.0(2)		
Ga1–Mn1–Mn2	51.97(4)	Mn1–Ga1–C1	142.2(2)
Ga1–Mn2–Mn1	55.07(4)	Mn2–Ga1–C1	144.7(2)
Ga2–Mn1–Mn2	56.63(4)	Mn1–Ga2–C2	148.5(2)
Ga2–Mn2–Mn1	51.39(4)	Mn1–Ga2–C2	139.2(2)
Mn1–Ga1–Mn2	72.96(5)		
Mn1–Ga2–Mn2	71.98(5)		
Compound 3			
Ga1–Fe1	239.03(6)	Ga1–C1	198.1(3)
Ga1–Fe3	240.29(6)	Ga2–C2	198.3(3)
Ga2–Fe1	239.49(7)	Fe1–Fe2	277.85(7)
Ga2–Fe2	239.60(6)	Fe1–Fe3	276.51(7)
		Fe2–Fe3	266.61(8)
Fe1–Ga2–Fe2	70.89(2)	Fe1–Fe2–Fe3	61.00(2)
Fe1–Ga1–Fe3	70.46(2)	Fe1–Fe3–Fe2	61.51(2)
Fe2–C9–Fe3	84.7(1)	Fe2–Fe1–Fe3	57.49(2)
C1–Ga1–Fe1	147.46(8)	C2–Ga2–Fe1	145.08(9)
C1–Ga1–Fe3	142.00(8)	C2–Ga2–Fe2	143.88(9)



red solution was obtained, from which after evaporation and recrystallization from cyclopentane dark red crystals of the iron gallium derivative **3** were isolated in a yield of only 33%. Compound **3** revealed a singlet in the ^1H NMR spectrum at δ 0.36. The carbon atom attached to gallium was observed at δ 58.1 in the ^{13}C NMR spectrum. As discussed above, similar shifts were detected for InR complexes^{5–7} or for the compound $\text{Ni}[\text{GaC}(\text{SiMe}_3)_3]_4$.⁹ No signal was resolved for the carbonyl carbon atoms at room temperature, but upon cooling to 218 K five resonances were observed in accordance with the solid state structure, as discussed below and schematically shown in eqn. (2). One singlet at a very low field (δ 254) was assigned to a bridging carbonyl group. The terminal CO ligands resonated at δ 217 and 213 in accordance with two chemically different Fe atoms and showed an intensity ratio of one to two. Both signals showed a further splitting into two resonances owing to the axial arrangement of two CO ligands and the location of one CO group in the molecular plane. At room temperature a fast exchange seems to equilibrate the resonances. CO stretching vibrations in the IR spectra in the range between 1956 and 2064 cm^{-1} and at 1836 cm^{-1} also showed that compound **3** has terminal and bridging CO ligands and that its structure must be different from that of the corresponding iron indium compound containing exclusively terminally co-ordinated CO

Table 2 Crystal data, data collection parameters and structure refinement of compounds **2** and **3**

	2 ·C ₅ H ₁₀	3 ·0.5C ₆ F ₅ H
Formula	C ₃₃ H ₆₄ Ga ₂ Mn ₂ O ₈ Si ₆	C ₃₃ H ₅₄ F _{2.5} Fe ₃ Ga ₂ O ₁₀ Si ₆
Crystal system	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$
<i>Z</i>	4	2
<i>T</i> /K	193	213
<i>D</i> /g cm ^{−3}	1.404	1.531
<i>a</i> /pm	2123.02(17)	938.53(9)
<i>b</i> /pm	947.67(4)	1475.7(2)
<i>c</i> /pm	2377.15(18)	1911.8(2)
<i>α</i> /°		75.71(2)
<i>β</i> /°	95.390(9)	80.740(10)
<i>γ</i> /°		74.490(10)
<i>U</i> /10 ^{−30} m ³	4761.5(6)	2459.7
<i>μ</i> /mm ^{−1}	1.830	2.146
Crystal size/mm	1.2 × 0.15 × 0.04	1.6 × 0.4 × 0.2
Independent reflections	8757	8915
Number of reflections [<i>F</i> > 4σ(<i>F</i>)]	3947	6612
Parameters	453	532
<i>R</i>	0.0521	0.0331
<i>wR</i> 2	0.1603	0.0875
<i>ρ</i> /10 ³⁰ e m ^{−3}	0.959/−0.699	0.627/−0.536

Programs SHELXL-93, SHELXTL;¹⁹ solutions by direct methods, full matrix refinement with all independent structure factors. STOE IPDS diffractometer, graphite monochromated Mo-Kα radiation.

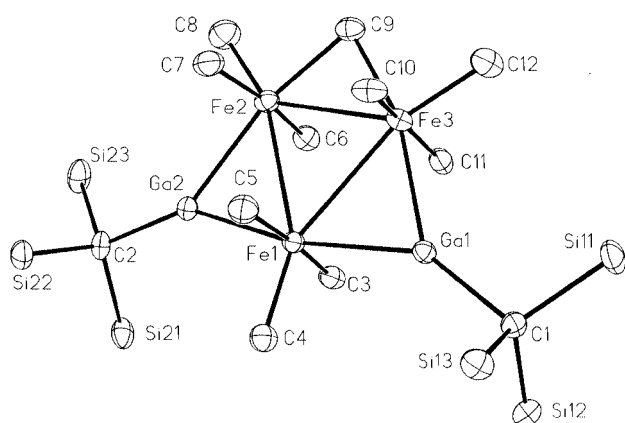


Fig. 2 Molecular structure and numbering scheme of compound **3**; the thermal ellipsoids are drawn at the 40% probability level; methyl groups are omitted for clarity.

groups (Chart 1). Owing to the low solubility of **3**, we did not succeed in determining its molar mass in solution. A violet compound of an unknown constitution was formed when **3** was treated with a further equivalent of GaR in boiling *n*-hexane in order to replace the last bridging CO ligand. This product was insoluble in solvents of different polarity such as cyclopentane or acetonitrile and therefore could not be purified and characterized up to now.

The molecular structure of **3** is depicted in Fig. 2. In contrast to the iron indium derivative described above (Chart 1), it is not isostructural to the starting carbonyl complex with only one Fe₂ couple bridged by two ligands. Instead, all three edges of the Fe₃ triangle are bridged, one by a carbonyl group and two by the GaR ligands. Thus, a rare example of a triiron compound is formed, in which the Fe₃ core is bridged by three μ-ligands.¹⁵ This unusual structure may be determined by steric factors, and the short Ga–Fe and Ga–C distances force the GaR groups to occupy different Fe–Fe edges. In the case of the common bridging of only one edge, the approach of the bulky C(SiMe₃)₃ substituents would result in considerable steric stress in the molecule, which owing to the longer separations of the central atoms is much smaller with the indium analogue. The molecular core of **3** comprising the atoms Fe1, Fe2, Fe3, Ga1, Ga2 and C9 of the bridging carbonyl group is almost planar, and the

largest deviation of that plane is observed for the carbonyl carbon atom C9 with 19.8 pm. The gallium atoms have a planar co-ordination sphere (sum of the angles Ga1, 360.0°; Ga2 359.9°).

The Fe–Fe distance of the carbonyl bridged edge (266.6 pm, Table 1) is similar to that of the carbonyl bridged Fe₂ couple in Fe₃(CO)₁₂ (268 pm).¹⁶ But the GaR bridged sides are much more elongated to 277.2 pm on average, which may be caused by the larger covalent radius of gallium compared to that of carbon and the long Fe–Ga bonds. A similar lengthening was observed for InR bridged Fe₂ groups.^{6,7} The Fe–Ga distances (239.6 pm on average) are similar to those observed for some other iron gallium complexes.¹⁷ The bond lengths between the Fe atoms and the C atoms of the terminally co-ordinated CO groups differ systematically, and those CO ligands which are in plane with the Ga atoms have Fe–C distances shortened by 4 pm compared to those including the ligands in axial positions (180.4 pm on average). All are similar to those observed for Fe₃(CO)₁₂.¹⁶ As expected, the Fe–C distances to the bridging carbonyl group are much longer (197.9 pm). The Ga–C bond lengths (**2**, 199.3 pm; **3**, 198.2 pm) are considerably shortened compared to those of the starting compound **1** (208 pm;¹ of the monomer in the gas phase: 206 pm³), which may be interpreted in terms of a higher oxidation state at the gallium atoms and a more ionic gallium to transition metal interaction as discussed recently.^{11,18}

Experimental

All procedures were carried out under purified argon in dried solvents (*n*-hexane and cyclopentane over LiAlH₄, toluene over Na/benzophenone). Compound **1** was synthesized as described in ref. 1. The commercially available carbonyls Mn₂(CO)₁₀ and Fe₃(CO)₁₂ were used without further purification.

Syntheses

Octacarbonylbis[μ-tris(trimethylsilyl)methylgallio]dimanganese 2. A solution of the tetragallium compound **1** (0.215 g, 0.179 mmol) and Mn₂(CO)₁₀ (0.139 g, 0.357 mmol) in 40 ml of toluene was heated to 60 °C for 18 h. The mixture adopted a bright orange colour, and very small quantities of an unknown colourless substance precipitated. After filtration, toluene was removed *in vacuo*, and the residue was recrystallized from *n*-hexane. Orange needles of **2** were obtained at

–30 °C (0.058 g, 17%). Mp (argon, sealed capillary) 205 °C (decomp.) (Found: Ga, 14.5%, Mn, 11.6%; $C_{28}H_{54}Ga_2Mn_2O_8Si_6$ requires Ga, 14.8%, Mn, 11.7%); δ_H (C_6D_6 , 300 MHz) 0.44 (s, $SiMe_3$); δ_C (C_6D_6 , 100.6 MHz, 298 K) 218.2 (CO), 48.8 (GaC), 6.3 ($SiMe_3$); $\tilde{\nu}_{max}/cm^{-1}$ (CsBr, paraffin) 2044m, 2014 (sh), 1999s, 1977s, 1965s, 1944vs, 1920s νCO ; 1463vs, 1377vs paraffin; 1301m, 1263s, 1248s δCH_3 ; 1170vw, 1155vw, 1077vw νCC (solvent); 849vs, 788m, 721m $\rho CH_3(Si)$; 677m $\nu_{as}SiC$; 640s, 622s ν_sSiC ; 486vw νGaC ; 394vw, 305vw δSiC ; λ_{max}/nm (*n*-hexane) ($\epsilon/dm^3 mol^{-1} cm^{-1}$): 225 (5000), 250 (7400), 280 (7100), 465 (1300).

(μ -Carbonyl-2:3 κ^2C)nonacarbonyl-1 κ^3C ,2 κ^3C ,3 κ^3C -bis-[μ -tris(trimethylsilyl)methylgallio-1:2 κ^2Ga ; 1:3 κ^2Ga]triiron 3. A mixture of 0.142 g (0.282 mmol) of $Fe_3(CO)_{12}$ and 0.179 g (0.149 mmol) of tetragallane(4) **1** in 40 ml of *n*-hexane was heated under reflux for 3 h. The colour changed to wine-red. The solvent was removed *in vacuo*, the residue was dissolved in cyclopentane and filtered. After concentration of the filtrate and cooling of the solution to –50 °C a red, amorphous solid of **3** was isolated (0.097 g, 33%). Mp (argon, sealed capillary) 155 °C (decomp.) (Found: Ga, 13.8%, Fe, 15.5%; $C_{30}H_{54}Fe_3Ga_2O_{10}Si_6$ requires Ga, 13.3%, Fe, 16.0%); δ_H (C_6D_6 , 300 MHz) 0.36 ($SiMe_3$); δ_C (D_8 -toluene, 100.6 MHz, 218 K) 254.4 (μ -CO), 217.2 (axial CO at Fe3), 216.7 (equatorial CO at Fe3), 213.4 (axial CO at Fe1 and Fe2), 213.0 (equatorial CO at Fe1 and Fe2), 58.1 (GaC), 5.2 ($SiMe_3$); $\tilde{\nu}_{max}/cm^{-1}$ (CsBr, paraffin) 2064m, 2020s, 2000s, 1984s, 1956s νCO (terminal); 1836s νCO (bridging); 1464vs, 1377vs paraffin; 1304w, 1263m, 1253m δCH_3 ; 1115m, 1084m, 1045m; 918w, 847vs, 797m, 721m $\rho CH_3(Si)$; 677m, 654m $\nu_{as}SiC$; 623vs, 613vs ν_sSiC ; 548s, 513m, 482m, 467m νGaC , νFeC ; 386w, 343vw δSiC ; λ_{max}/nm (*n*-hexane) ($\epsilon/dm^3 mol^{-1} cm^{-1}$): 252 (40000), 310 (sh, 16000), 520 (8500); *m/z* (FD)(%) 1047.7 (85), 1049.0 (100), 1050.0 (90), 1051.0 (35) all M^+ in accordance with a calculated isotope pattern.

X-Ray crystallography

Single crystals were obtained by slow cooling of solutions in cyclopentane (**2**) and pentafluorobenzene (**3**). Crystal data and structure refinement parameters are given in Table 2. One cyclopentane molecule was found for each formula unit of **2**, its carbon and hydrogen atoms were refined isotropically. The unit cell of **3** enclosed one molecule of pentafluorobenzene, which was located on a crystallographic center of symmetry. It showed a disorder of the fluorine atoms, which were anisotropically refined with occupancy factors of 5/6. The hydrogen atom was not considered.

CCDC reference number 186/1810.

See <http://www.rsc.org/suppdata/dt/a9/a909658b/> for crystallographic files in .cif format.

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