Synthetic and Structural Studies on Organotransition Metal-Gallium Complexes

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The transition metal-gallium complexes [Ga(ML$_n$)$_3$] [where ML$_n$ = Fe(CO)$_2$(η-C$_5$H$_5$), Mo(CO)$_3$(η-C$_5$H$_5$), Co(CO)$_3$(PPh$_3$), and Mn(CO)$_5$] have been synthesised by salt elimination between GaCl$_3$ and M$^\mathrm{I}$(ML$_n$) (M$^\mathrm{I}$ = Na/K). The iron complex [Ga{Fe(CO)$_2$(η-C$_5$H$_5$)}$_3$] (**1**) has been characterised by X-ray crystallography and shown to contain a planar, three-coordinate gallium centre bound to three Fe(CO)$_2$(η-C$_5$H$_5$) fragments by unsupported Ga–Fe bonds [av. 2.444(1) Å]. A partial structure determination of [Ga{Mo(CO)$_3$(η-C$_5$H$_5$)}$_3$] (**5**) is consistent with a trigonal-planar GaMo$_3$ core. Brief mention is also made of two chloro complexes [GaCl(ML$_n$)$_2$] [ML$_n$ = Fe(CO)$_2$(η-C$_5$H$_5$) and Co(CO)$_3$(PPh$_3$)].

Compounds containing both gallium and a transition metal are currently of interest as potential single-source precursors to binary intermetallic phases. Such interest stems from the fact that certain phases are useful as Schottky barriers and Ohmic contacts to 13–15 semiconductors and, in this regard, we note a recent paper by Chen et al.[1] concerning the chemical vapour deposition of CoGa and PtGa$_2$ from precursor molecules containing these respective elements. Nevertheless, such applications are likely to be limited at present by the relative paucity of known compounds containing gallium and a transition metal.

The most extensive studies on transition metal-gallium complexes have been carried out by Haupt and coworkers over a number of years. The compounds which have been described are [Mn$_2$(CO)$_8${μ-GaMn(CO)$_5$}$_2$][2], [Re$_2$(CO)$_8${μ-GaRe(CO)$_5$}$_2$][3], [PPh$_4$]$_2$[Mn$_2$(CO)$_8$(μ-GaX$_2$)$_2$] (X = Cl, Br)[4], [Re$_2$(CO)$_4$(PPh$_3$)$_2$(μ-I)$_2${μ-GaRe(CO)$_4$(PPh$_3$)}][5], Na[Cl$_{4-n}$Ga{Mn(CO)$_5$}$_n$] (n = 1–3)[6], and [Re$_3$(CO)$_9$(PPh$_3$)$_3$(μ-Cl)$_3${μ_3-GaRe(CO)$_4$(PPh$_3$)}], [Re$_2$(CO)$_4$(PPh$_3$)$_2$(μ-Br)$_2${μ-GaRe(CO)$_4$(PPh$_3$)}], and [Re$_2$(CO)$_6$(PPh$_3$)$_2$(μ-I)(μ-GaI$_2$)][7]. Most of these complexes, together with the indium analogues, have also been described in a recent review[8]. The manganese complex [Mn(CO)$_5$(GaCl$_2$ · THF)] has been reported[9], and a range of Co(CO)$_4$-gallium complexes have been described by Patmore and Graham[10], eg. [X$_2$GaCo(CO)$_4$(THF)], [XGa{Co(CO)$_4$}$_2$(THF)], and [(acac)Ga{Co(CO)$_4$}$_2$]. Other examples include [Fe$_2$(CO)$_8${μ-GaC$_2$H$_3$(THF)}$_2$][11], [Ph$_3$Ga(ML$_n$)]$^-$ [ML$_n$ = Co(CO)$_4$, Mn(CO)$_5$, W(CO)$_3$(η-C$_5$H$_5$) and Fe(CO)$_2$(η-C$_5$H$_5$)][12], [Pt(Cy$_2$PCH$_2$CH$_2$PCy$_2$)(GaR$_2$)(R)] (R = neopentyl)[13], [Ga{W(CO)$_3$(η-C$_5$H$_5$)}$_3$][14], [GaMe$_2${W(CO)$_3$(η-C$_5$H$_5$)}][15], [GaI$_2$(Et$_2$O){Mo(CO)$_3$(η-C$_5$H$_4$Me)}], and [Ga(η^1-C$_5$H$_4$Me)$_2$(py){Fe(CO)$_2$(η-C$_5$H$_5$)}][16] and a range of transition metal-gallium-porphyrin complexes[17].

Herein we report details on some of our own studies on transition metal-gallium complexes.

Results and Discussion

The reaction between GaCl$_3$ and three equivalents of Na[Fe(CO)$_2$(η-C$_5$H$_5$)] afforded, after workup and recrystallisation from THF/hexane mixtures, dark red crystals of the triiron-gallium complex **1**, and it was evident from a solution infrared spectrum [Table 1, Figure 1(a)] that this complex was very similar to the indium analogue **2**[18]. The molecular structure of **1**, as determined by X-ray crystallography, is

Table 1. Solution infrared data for the complexes[a,b]

	Compound	ν(CO)/cm^{-1}
1	[Ga{Fe(CO)$_2$(η-C$_5$H$_5$)}$_3$]	1987 m, 1965 s, 1920 s
5	[Ga{Mo(CO)$_3$(η-C$_5$H$_5$)}$_3$]	2025 s, 1933 s, br[c] 2024 s, 2008 m, 1935 s, br[d] 2022 s, 2007 m, 1933 s, br 2023 s, 2008 m, 1933 s, br, 1899 m, 1781 m[e] 2023 m, 1929 s, 1897 m, 1779 m[f]
7	[Ga{Co(CO)$_3$(PPh$_3$)}$_3$]	2000 w, 1954 s
10	[Ga{Mn(CO)$_5$}$_3$]	2034 m, 2017 w, 1974 s, 1935 m, 1888 w
11	[GaCl{Fe(CO)$_2$(η-C$_5$H$_5$)}$_2$]	2047 w, 1990 s, 1969 s, 1932 s, 1917 s
12	[GaCl{Co(CO)$_3$(PPh$_3$)}$_2$]	2026 w, 2007 w, 1954 s

[a] Measured in THF solution unless otherwise stated. – [b] s = strong, m = medium, w = weak, br = broad. – [c] Measured in CH$_2$Cl$_2$ solution. – [d] Measured in toluene solution. The values reported for **5** in this solvent in KBr in ref.[15] are 1964 s, 1905 s, 1889 w. These are rather different from our values and from those reported for the tungsten complex [Ga{W(CO)$_3$(η-C$_5$H$_5$)}$_3$][14] in benzene; 2020 s, 1940 s. For the indium complexes, values for the Mo and W compounds do not differ by more than 5 cm^{-1}[19a]. – [e] Measured in acetone solution. – [f] Measured in MeCN solution.

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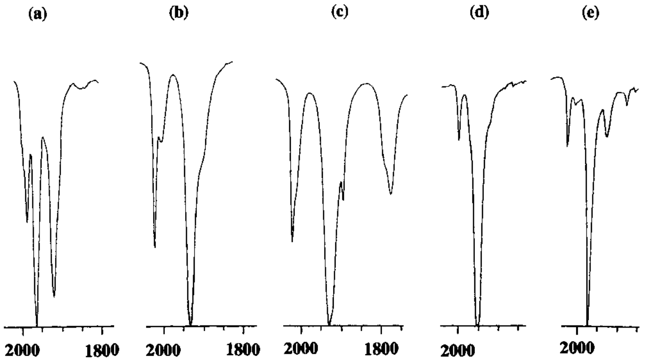


Figure 1. Solution infrared spectra in the carbonyl region obtained in CaF_2 cells for the complexes. (a) **1** in THF, (b) **5** in THF, (c) **5** in MeCN, (d) **7** in THF, (e) **10** in THF

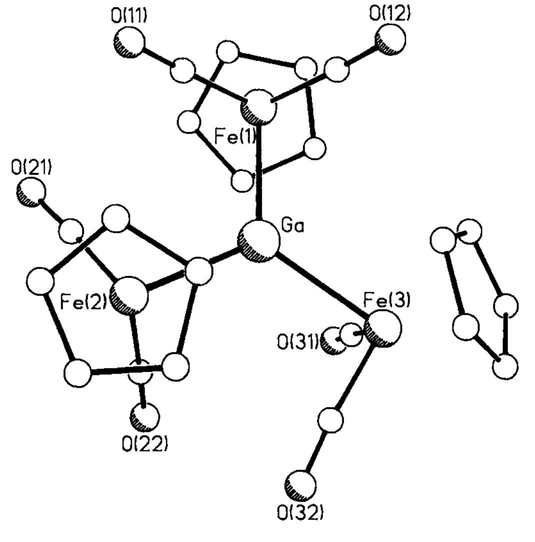


Figure 2. A view of the molecular structure of **1** showing the atom numbering scheme adopted. Hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [deg]: Ga–Fe(1) 2.440(1), Ga–Fe(2) 2.436(1), Ga–Fe(3) 2.456(1); Fe(1)–Ga–Fe(2) 119.7(1), Fe(1)–Ga–Fe(3) 120.9(1), Fe(2)–Ga–Fe(3) 119.4(1)

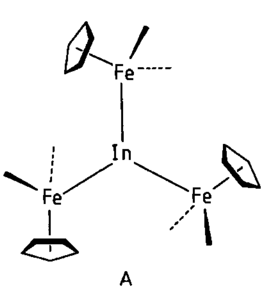
shown in Figure 2 and atomic positional parameters are presented in Table 2.

[Ga{Fe(CO)$_2$(η-C$_5$H$_5$)}$_3$] **1**	[In{Fe(CO)$_2$(η-C$_5$H$_5$)}$_3$] **2**
[In{Mo(CO)$_3$(η-C$_5$H$_5$)}$_3$] **3**	[Te{Mn(CO)$_2$(η-C$_5$H$_5$)}$_3$] **4**

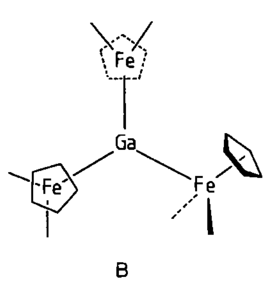
Table 2. Atomic coordinates (× 10^4) and equivalent isotropic thermal parameters (Å^2 × 10^3) for **1**. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} matrix

	x	y	z	U_{eq}
Ga	3760.0(1)	1923.7(3)	3044.4(2)	42.8(1)
Fe(1)	3785.7(2)	3197.1(4)	1808.5(3)	53.9(2)
Fe(2)	4056.9(2)	2784.5(4)	4555.2(2)	47.9(1)
Fe(3)	3419.5(2)	−203.3(4)	2781.6(2)	49.9(1)
C(11)	4313(1)	4021(3)	2567(2)	79(2)
O(11)	4664(1)	4576(3)	3046(2)	133(2)
C(12)	4217(1)	2164(3)	1618(2)	71(1)
O(12)	4518(1)	1520(3)	1476(2)	112(2)
C(13)	3282(2)	3437(4)	457(2)	92(2)
C(14)	3390(2)	4594(4)	876(3)	102(2)
C(15)	3205(2)	4568(3)	1584(3)	91(2)
C(16)	2976(1)	3405(3)	1593(2)	78(2)
C(17)	3032(1)	2693(3)	903(2)	77(1)
C(21)	3901(1)	4289(3)	4134(2)	64(1)
O(21)	3818(1)	5298(2)	3913(1)	89(1)
C(22)	3410(1)	2512(3)	4479(2)	64(1)
O(22)	2968(1)	2363(3)	4438(2)	103(1)
C(23)	4757(1)	3238(4)	5632(2)	98(2)
C(24)	4881(1)	2816(3)	4902(2)	84(1)
C(25)	4705(1)	1611(3)	4734(2)	72(1)
C(26)	4474(1)	1282(3)	5328(2)	74(1)
C(27)	4512(1)	2303(4)	5891(2)	87(2)
C(31)	2802(1)	510(3)	2304(2)	65(1)
O(31)	2387(1)	931(3)	1987(2)	107(1)
C(32)	3375(1)	−309(3)	3834(2)	69(1)
O(32)	3350(1)	−475(3)	4519(1)	105(1)
C(33)	4102(1)	−585(3)	2512(2)	72(1)
C(34)	3652(1)	−586(3)	1705(2)	69(1)
C(35)	3308(1)	−1525(3)	1769(2)	87(2)
C(36)	3539(2)	−2086(3)	2598(2)	95(2)
C(37)	4027(2)	−1504(3)	3062(2)	93(2)

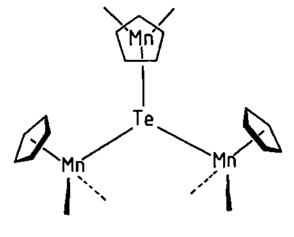
The structure of **1** comprises a gallium atom in a trigonal-planar coordination environment (sum of angles 360.0°; Ga lies 0.017 Å from the Fe_3 plane) bound to three Fe(CO)$_2$(η-C$_5$H$_5$) fragments by unsupported Ga–Fe bonds (av Ga–Fe 2.444(1) Å, cf. 2.4272(9) Å in [Ga(η^1-C$_5$H$_4$Me)$_2$(py){Fe(CO)$_2$(η-C$_5$H$_5$)}][16]). In ref.[18] we postulated, on the basis of electronic arguments, that a likely structure for **2** was one with C_{3h} symmetry (formula **A**), analogous to the known structure of [In{Mo(CO)$_3$(η-C$_5$H$_5$)}$_3$] (**3**)[19]. These arguments were based on the possibility of π-bonding between filled metal d orbitals and the vacant 5p orbital on indium and are described in detail for **3** in ref.[19b]. Specifically, for the case of **2**, the orbital best disposed toward π-bonding, as described by Hoffmann et al.[20], is the one which bisects the symmetry plane of the Fe(CO)$_2$(η-C$_5$H$_5$) fragment, and it was on this basis that the structure of **2** was postulated. However, it is clear from Figure 2 that the structure of **1** has much lower symmetry than C_{3h} (see **B**) with no obvious orientational preference observed for the Fe(CO)$_2$(η-C$_5$H$_5$) fragments with respect to the conformations about the Ga–Fe bonds. Although this does not mean that the structure of **2** is the same, the sim-



A



B



C

ilarity of the infrared spectra for the two complexes [Figure 1(a) for **1**, Figure (a) in ref.[18] for **2**] shows that they are clearly very similar in solution. In fact, on the basis of calculations described in ref.[19b], we no longer think that π-bonding effects are important in these types of compound and therefore that orientational preferences arising from electronic factors are not to be expected. In this regard, we note the isoelectronic manganese-tellurium complex $[Te\{Mn(CO)_2(\eta\text{-}C_5H_5)\}_3]$ (**4**) described by Herberhold et al.[21] which is similar in most respects to **1** but differs slightly in the conformations about the Te – Mn bonds as shown in **C**.

The origin of this difference is unclear but we note that molecular structures differing *only* with respect to the conformations about single M – M bonds may be observed even for the *same* compound, e. g. the two different polymorphs of $[Tl\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_3]$[19b] for one of which the molecule has a structure similar to **A** whereas the other is of type **B**. We shall return to the matter of the electronic structure of **1**, **4** and related ruthenium-indium complexes in more detail in a later paper.

The reaction between $GaCl_3$ and three equivalents of $Na[Mo(CO)_3(\eta\text{-}C_5H_5)]$ afforded the yellow crystalline complex $[Ga\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_3]$ (**5**). Compound **5** has been reported by Oliver and coworkers[15] having been synthesised from the reaction between $GaMe_3$ and three equivalents of the molybdenum hydride $[MoH(CO)_3(\eta\text{-}C_5H_5)]$. We tried to characterise **5** by X-ray crystallography using well formed yellow crystals obtained from CH_2Cl_2/hexane mixtures but, as described in the Experimental Section, the structure is disordered and only the $GaMo_3$ core could be resolved. This, however, was sufficient to establish a trigonal-planar arrangement analogous to $[Ga\{W(CO)_3(\eta\text{-}C_5H_5)\}_3]$ (**6**)[14] and the indium and thallium derivatives $[E\{M(CO)_3(\eta\text{-}C_5H_5)\}_3]$ (E = In, Tl; M = Cr, Mo)[19b]. As we describe in detail in ref.[19b], the properties of $[In\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_3]$ (**3**) in solution are very dependent on the solvent used. Specifically, compound **3** is undissociated in toluene, CH_2Cl_2 and THF but partially dissociated into the ionic form $[In(solv)_x\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]^+$ $[Mo(CO)_3(\eta\text{-}C_5H_5)]^-$ in acetone and MeCN. The gallium complex **5** has similar properties in all of the above solvents although it dissociates to a slightly lesser extent than **3** in acetone judging by the intensity of the absorption at ≈ 1780 cm^{-1} due to $[Mo(CO)_3(\eta\text{-}C_5H_5]^-$. Representative spectra in THF and MeCN are shown in Figure 1(b) and (c), respectively; numerical data for all solvents are given in Table 1[22].

$[Ga\{M(CO)_3(\eta\text{-}C_5H_5)\}_3]$ $[E\{Co(CO)_3(PPh_3)\}_3]$
5: M = Mo **7**: E = Ga
6: M = W **8**: E = In

The reaction between $GaCl_3$ and three equivalents of $K[Co(CO)_3(PPh_3)]$ afforded the orange crystalline complex **7** which was characterised by infrared [Table 1, Figure 1(d)] and analytical data. Compound **7** is similar in most respects to the indium analogue **8** which we have previously described[23] although the complex ^{31}P-NMR spectra obtained for **8**, which were indicative of several species present in equilibrium in solution, were not observed for **7** for which only one signal was seen. This is consistent with gallium complexes being slightly less prone to dissociation than their indium analogues (cf. **5** vs. **3** in acetone, see above).

The complex $[Ga\{Co(CO)_4\}_3]$ (**9**), in contrast to the phosphane derivative, does not seem to be particularly stable. Patmore and Graham reported that they were unable to obtain **9** by halide displacement from GaX_3 by $[Co(CO)_4]^-$[10] although in a later report by Kalbfus et al.[24] this complex was obtained by this route using $GaBr_3$. The proposed structure for **9**[24] is, in our opinion, unlikely in view of the known structure of the indium analogue which contains a trigonal-planar indium centre[25], but the apparent thermal instability of **9** is in line with our own observations that reactions carried out to synthesise **9** are difficult to work up and readily afford $[Co_4(CO)_{12}]$. It is not clear why **9** should be so much less stable than indium and thallium analogues.

$[Ga\{Co(CO)_4\}_3]$ $[Ga\{Mn(CO)_5\}_3]$
9 **10**

A great deal has been published on the indium and thallium complexes $[E\{Mn(CO)_5\}_3]$[8] (E = In, Tl) but much less on the gallium derivative **10**. The most relevant previous report with regard to **10** is by Haupt et al.[6] but these authors found that the reaction between $GaCl_3$ and three equivalents of $Na[Mn(CO)_5]$ in THF afforded the chloroanionic complex $Na[GaCl\{Mn(CO)_5\}_3]$, i. e. **10** could not be obtained free of chloride. We studied this reaction which is described in the Experimental Section and found that an orange complex could be extracted into Et_2O which, upon cooling, yielded well-formed orange crystals. Infrared data [Table 1, Figure 1(e)] were consistent with a high-symmetry structure containing $Mn(CO)_5$ groups and the analytical data support the formula for **10**. The solubility of this material in Et_2O is also consistent with a neutral as opposed to an ionic compound but we were unable to obtain X-ray structural data because of the extremely facile loss of solvent of crystallisation from otherwise excellent looking crystals.

Finally, we mention two reactions of the above compounds which afford complexes of the general formula $[GaCl(ML_n)_2]$ although we have not sought to explore reactivity to any great extent at this stage nor to synthesise a range of halo species as we have done for indium. Compounds **1** and **7** react with $GaCl_3$ according to equations (1), (2) to give the complexes **11** and **12**.

$$\underset{\mathbf{1}}{2[Ga\{Fe(CO)_2(\eta\text{-}_5H_5)\}_3]} + GaCl_3 \longrightarrow \underset{\mathbf{11}}{3[GaCl\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]} \quad (1)$$

$$\underset{\mathbf{7}}{2[Ga\{Co(CO)_3(PPh_3)\}_3]} + GaCl_3 \longrightarrow \underset{\mathbf{12}}{3[GaCl\{Co(CO)_3(PPh_3)\}_2]} \quad (2)$$

Infrared data, presented in Table 1, are very similar to the indium analogues $[InCl\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$[26] and $[InCl\{Co(CO)_3(PPh_3)\}_2]$[23] whilst the mass spectrum of **11** is also consistent with the dimeric structure observed for the indium complex[26].

Further studies are in progress on aspects of reactivity and, in particular, on the potential of these compounds as single-source precursors to materials containing the respective elements.

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Experimental

All experiments were performed under dry, oxygen-free dinitrogen using standard Schlenck techniques. All solvents were dried and distilled over appropriate drying agents immediately prior to use. – IR: Nicolet 20 SXB FTIR spectrophotometer. – MS: Kratos MS80 instrument, EI mode, 70 eV. – Microanalytical data: University of Newcastle. – ^{31}P NMR: Bruker WM 300 spectrometer, 121.49 MHz, referenced to 85% H_3PO_4.

All starting materials were either procured commercially or made by standard literature methods referenced where appropriate.

Preparation of $[Ga\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_3]$ (**1**): A stirred solution of $Na[Fe(CO)_2(\eta\text{-}C_5H_5)]$, derived from a Na/Hg reduction of $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$ (0.316 g, 0.894 mmol), in THF (20 ml) was cooled to $-78\,^{\circ}C$ and maintained at this temp. To this was added a solution of $GaCl_3$ (0.105 g, 0.596 mmol) in THF (4 ml) over a period of a few minutes. After complete addition, the turbid yellow-brown solution was allowed to warm to room temp. and stirring was continued overnight, after which time a marked increase in the intensity of the colour of the solution was observed. Removal of the THF by vacuum afforded a dark yellow-brown residue which was extracted with CH_2Cl_2 (20 ml). The solution was filtered through Celite. After reduction of the filtrate solvent volume to about 5 ml, crystallisation was effected by solvent diffusion using an overlayer of hexane (30 ml) over a period of several days at $-30\,^{\circ}C$. This afforded **1** as dark brown crystals, 0.11 g (31%). Crystals suitable for X-ray diffraction were obtained by solvent diffusion from $ClCH_2CH_2Cl$/hexane mixtures over several days at $-30\,^{\circ}C$. – MS: *m/z* 572 [P – 1 CO] (P = $Ga\{Fe(CO)_2(C_5H_5)\}_3$); 544 [P – 2 CO], 516 [P –3 CO], 460 [P – 5 CO], 432, [P – 6 CO], 423 [P – $Fe(CO)_2(C_5H_5)$], 367 [P – ($Fe(CO)_2(C_5H_5)$ + 2 CO)].

$C_{21}H_{15}Fe_3GaO_6$ (600.6) Calcd. C 41.99 H 2.52
Found C 41.69 H 2.17

Preparation of $[Ga\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_3]$ (**5**): A stirred solution of $Na[Mo(CO)_3(\eta\text{-}C_5H_5)]$, derived from a Na/Hg reduction of $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ (0.438 g, 0.894 mmol), in THF (20 ml) was cooled to $-78\,^{\circ}C$ and maintained at this temp. To this a solution of $GaCl_3$ (0.105 g, 0.596 mmol) in THF (4 ml) was added over a period of a few minutes. After complete addition, the turbid yellow solution was allowed to warm to room temp. with continuous stirring. No observable colour changes were apparent during the first hour. Stirring was continued for a further 16h, after which time the solution had darkened from pale yellow to very intense yellow. The THF was removed by vacuum, and the dark yellow-brown residue was extracted in CH_2Cl_2 (30 ml) and the solution filtered through Celite, affording a dark yellow-brown filtrate from which yellow needle-like crystals were obtained after reduction of the solvent volume to about 6 ml and diffusion of an overlayer of hexane (40 ml) over a period of several days at $-30\,^{\circ}C$. Typical yields: 25%. – MS: *m/z* 721 [P – 3 CO] (P = $Ga\{Mo(CO)_3(C_5H_5)\}_3$), 665 [P – 5 CO], 637 [P – 6 CO], 609 [P – 7 CO], 581 [P – 8 CO], 553 [P – 9 CO].

$C_{24}H_{15}GaMo_3O_9$ (804.9) Calcd. C 35.81 H 1.88
Found C 35.83 H 1.61

Preparation of $[Ga\{Co(CO)_3(PPh_3)\}_3]$ (**7**): A solution of $K[Co(CO)_4]$, derived from a KOH reduction of $[Co_2(CO)_8]$ (0.513 g, 1.500 mmol), in THF (20 ml)[27] was refluxed with PPh_3[28] (0.787 g, 3.000 mmol) for 45 min. The resulting pale yellow solution of $K[Co(CO)_3(PPh_3)]$ was cooled to $0\,^{\circ}C$ (ice-bath) and stirred as a solution of $GaCl_3$ (0.176 g, 1.000 mmol) in THF (5 ml) was added over a period of a few minutes. After complete addition, the pale yellow reaction solution was allowed to warm to room temp. with continuous stirring for 8h, during which time the solution slowly became turbid and turned dark orange in colour. Removal of the THF by vacuum afforded an oily orange residue which was extracted with CH_2Cl_2 (30 ml). The solution was filtered through Celite. Reduction of the solvent volume to about 6 ml followed by crystallisation by solvent diffusion using an overlayer of hexane (40 ml) over a period of several days at $-30\,^{\circ}C$ afforded an orange powder and an intensely coloured yellow mother liquor. Typical yields: 25%. – ^{31}P NMR (CD_2Cl_2): δ 57.6.

$C_{63}H_{45}Co_3GaO_9P_3$ (1285.4) Calcd. C 58.86 H 3.53
Found C 58.15 H 3.52

Preparation of $[Ga\{Mn(CO)_5\}_3]$ (**10**): A stirred solution of $Na[Mn(CO)_5]$, derived from a Na/Hg reduction of $[Mn_2(CO)_{10}]$ (0.970 g, 2.488 mmol), in THF (20 ml) was cooled to $-78\,^{\circ}C$ and maintained at this temp. To this was added a solution of $GaCl_3$ (0.292 g, 1.658 mmol) in THF (5 ml) over a period of a few minutes. After complete addition, the turbid yellow solution was allowed to warm to room temp. with continuous stirring for a further 16h. After this time the solution had changed colour from pale yellow to orange. Removal of the THF by vacuum afforded an oily orange residue which was extracted with Et_2O (60 ml). The solution was filtered through Celite. On reduction of the solvent volume, a solid started to drop out of the solution. The Et_2O was removed completely, and redissolution of the residue in THF (8 ml) afforded an orange solution over which hexane (60 ml) was layered. Solvent diffusion over a period of several days at $-30\,^{\circ}C$ afforded **10** as orange rods which very readily lost solvent on removal from the mother liquor. Recrystallisation either from a concentrated solution in Et_2O or by solvent diffusion using Et_2O/hexane mixtures afforded **10** as orange blocks which were unsuitable for X-ray diffraction studies due to facile loss of solvent. Recrystallisation from pyridine/hexane afforded an oil, and low solubility in MeCN, toluene, cyclohexane and CH_2Cl_2 precluded crystallisation from any of these solvent systems. Typical yields after recrystallisation: 33%.

$C_{15}O_{15}GaMn_3$ (654.7) Calcd. C 27.52 Found C 28.48

Preparation of $[GaCl\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (**11**): A solution of $GaCl_3$ (0.013 g, 0.072 mmol) in THF (1 ml) was added to a stirred solution of **1** (0.087 g, 0.145 mmol) in THF (10 ml). After 3 h the solution was reduced in volume by vacuum to about 5 ml. Hexane (30 ml) was layered over this solution, and crystallisation by solvent diffusion, over a period of days at $-30\,^{\circ}C$ afforded **11** as a red-orange crystalline solid, yield 0.075 g (75%). – MS: *m/z* 916 [$Ga_2Cl_2\{Fe(CO)_2(C_5H_5)\}_4$].

$C_{14}H_{10}ClFe_2GaO_4$ (459.1) Calcd. C 36.62 H 2.20
Found C 36.28 H 2.13

The cobalt complex **12** was prepared in an analogous manner from **7** and $GaCl_3$ and isolated in similar yield.

In all cases the yields quoted are for recrystallised material although the reactions undoubtedly proceed in much higher yield.

X-ray Crystallography

Crystal data for **1**: $C_{21}H_{15}Fe_3GaO_6$, M = 600.6, monoclinic, space group $C2/c$, a = 27.244(4), b = 10.813(2), c = 16.077(3) Å,

β = 112.25 (2)°, V = 4383.4 Å^3, Z = 8, d_{calc} = 1.820 g cm^{-3}, F(000) = 2384, μ = 3.19 mm^{-1} for Mo-K_α radiation (λ = 0.71073 Å), T = 295K. Measurements were made on a Stoe-Siemens diffractometer with graphite monochromator, from a crystal of size 0.35 × 0.38 × 0.62 mm, mounted in a capillary tube. Cell parameters were refined from 2Θ values (20–25°) of 32 reflections measured at $\pm\omega$. Intensities were measured by ω/Θ scans with on-line profile fitting[29]: 2Θ_{max} = 50° with index ranges h −32 to 32, k 0 to 12, l 0 to 19, together with most of two sets of equivalent reflections. Semiempirical absorption corrections were applied, with transmission factors in the range 0.272–0.324. 10994 measured reflections yielded 3863 unique data, 3427 of them with $F > 4\sigma_c(F)$ (σ_c from counting statistics only); R_{int} = 0.023.

The structure was determined by direct methods and refined by blocked-cascade least-squares on F, with weighting[30] $w^{-1} = \sigma^2(F) = \sigma^2_c(F) - 375 + 759G + 3224G^2 + 1550H - 1123H^2 - 4991GH$; $G = F_o/F_{\text{max}}$, $H = \sin\Theta/\sin\Theta_{\text{max}}$. Anisotropic thermal parameters were refined for non-H-atoms, isotropic H atoms were constrained to give C–H = 0.96 Å on ring angle external bisectors, with $U(H) = 1.2U_{\text{eq}}(C)$. Atomic scattering factors were taken from ref.[31]; extinction effects were insignificant. At convergence, R = 0.0286, R_w = 0.0248, S = 1.49 for 280 parameters, largest shift/e.s.d. = 0.013; all features in a final difference synthesis lay within ±0.4 eÅ^{-3}. SHELXS, SHELXTL[32] and local programs were used[33].

Crystal Data for **5**: $C_{24}H_{15}GaMo_3O_9$, M = 613.0, apparently hexagonal, a = 11.7167(8), c = 12.7227(10) Å, V = 1512.6 Å^3, Z = 2, d_{calc} = 1.767 g cm^{-3}, F(000) = 776, μ = 11.6 mm^{-1} for Cu-K_α radiation (λ = 1.54184 Å), T = 240K. Data were collected as for **1** (2Θ_{max} = 130°, maximum indices 13, 13, 14, with almost a complete sphere of data, total number of reflections = 5450, transmission factors 0.132–0.283). The Laue symmetry is apparently 6/*mmm*. Intensity statistics and the Patterson function are most consistent with space group $P\bar{6}2c$ (R_{int} = 0.045, 883 unique observed reflections without merging Friedel opposites). From the Patterson synthesis it was possible to locate Ga and Mo atoms in a perfect trigonal planar arrangement with Ga–Mo bond lengths of about 2.74 Å, but other atoms could not be found in subsequent difference syntheses.

The cell parameters are very similar to those of $[In\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_3]$ · THF, for which the space group is $P\bar{6}2c$[19b], but the two compounds are not isostructural, as is clear from comparisons of their Patterson functions and intensity data sets. It seems that the structure of **5** is either severely disordered or actually of lower true symmetry and only apparently hexagonal by twinning.

CAS Registry Numbers

1: 137008-62-9 / **5**: 63184-24-7 / **7**: 137008-61-8 / **10**: 137038-79-0 / **11**: 137008-60-7 / **12**: 137008-59-4 / $Na[Fe(CO)_2(\eta\text{-}C_5H_5)]$: 12152-20-4 / $Fe_2(CO)_4(\eta\text{-}C_5H_5)_2$: 12154-95-9 / $GaCl_3$: 13450-90-3 / $Na[Mo(CO)_3(\eta\text{-}C_5H_5)]$: 12107-35-6 / $Mo_2(CO)_6(\eta\text{-}C_5H_5)_2$: 60974-85-8 / $Co_2(CO)_8$: 10210-68-1 / $K[Co(CO)_3(PPh_3)]$: 67486-01-5 / $Na[Mn(CO)_5]$: 13859-41-1 / $Mn_2(CO)_{10}$: 10170-69-1

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