Complexes of a gallium heterocycle with transition metal dicyclopentadienyl and cyclopentadienylcarbonyl fragments, and with a dialkylmanganese compound†

Simon Aldridge, Robert J. Baker, Natalie D. Coombs, Cameron Jones,* Richard P. Rose, Andrea Rossin and David J. Willock

The reactivity of several transition metal half sandwich complexes towards an anionic gallium(I) heterocyclic complex, [K(tmeda)][Ga{[N(Ar)C(H)]$_2$}] (Ar = C$_6$H$_3$Pr$^i_2$-2,6), has been investigated. This has led to the anionic half sandwich complexes, [K(tmeda)][(C$_5$H$_4$R)M(CO)$_n$[Ga{[N(Ar)C(H)]$_2$}]] (M = V, R = H, n = 3; M = Mn, R = Me, n = 2; M = Co, R = H, n = 1), which crystallographic studies show to form dimers (M = Mn and Co) or a polymer (M = V) through bridging potassium cations. The metal–gallium bond lengths in all complexes are very short which, combined with some spectroscopic evidence, is suggestive of M–Ga π-bonding. Density functional theory studies of models of all complexes indicate that the level of back-bonding in these complexes is, however, minimal and of a similar order to that seen in analogous complexes incorporating neutral N-heterocyclic carbene ligands. Reactions of the metallocenes, [M(C$_5$H$_4$Me)$_2$] (M = V or Cr), with the digallane(4), [Ga{[N(Ar)C(H)]$_2$}]$_2$, have afforded the neutral complexes, [M(C$_5$H$_4$Me)$_2$Ga{[N(Ar)C(H)]$_2$}]], which are thought to be formed *via* an initial oxidative insertion of the transition metal centre into the Ga–Ga bond of the digallane. X-Ray crystallography shows the complexes to be monomeric. One (M = V) reacts with one equivalent of [K(tmeda)][Ga{[N(Ar)C(H)]$_2$}] to give the crystallographically characterised, anionic bis(gallyl)-complex, [K(tmeda)][V(C$_5$H$_4$Me)$_2$[Ga{[N(Ar)C(H)]$_2$}]$_2$]. For comparison, the reaction of [K(tmeda)][Ga{[N(Ar)C(H)]$_2$}] with [Mn{CH(SiMe$_3$)$_2$}$_2$] was carried out and gave the monomeric, anionic complex, [K(tmeda)][Mn{CH(SiMe$_3$)$_2$}$_2$[Ga{[N(Ar)C(H)]$_2$}]].

Introduction

The coordination chemistry of the N-heterocyclic carbene (NHC) class of ligand has been extensively explored and complexes of these heterocycles have found a variety of applications.[1] Of most note are transition metal–NHC complexes, many of which show high activity and/or selectivity as catalysts in a number of processes. This has led to NHCs being widely regarded as phosphine mimics, as they are strong σ-donors but very poor π-acids, a result of considerable N p-orbital lone pair overlap with the p-orbital of the carbene carbon. We are interested in preparing Group 13 metal(I) analogues of NHCs and comparing the coordination and further chemistry of the two ligand classes. Most success has come with the anionic five-membered heterocycle in **1**, which is valence isoelectronic with NHCs.[2] The s- and p-block coordination chemistry[3,4] of this heterocycle has shown similarities with that of NHCs in that it is very nucleophilic and can stabilise thermally labile fragments, *e.g.* indium hydrides. To date, the transition metal coordination chemistry of **1** has been limited to the iron carbonyl complex, **2**,[5]

and the nickel complexes, **3** and **4**.[6] Theoretical and spectroscopic studies on **2** and a model complex have shown that, although the p-orbital at the gallium centre interacts minimally with the nitrogen p-orbital lone pairs and is therefore effectively unoccupied, there is negligible Fe→Ga back-bonding in this complex. This is not surprising considering the likely high energy of the gallium p-orbital relative to the π* acceptor orbitals of the CO ligand *trans* to the heterocycle. A related bis(gallyl)–zirconium(III) complex, **5**, has also been accessed *via* the oxidative insertion of the
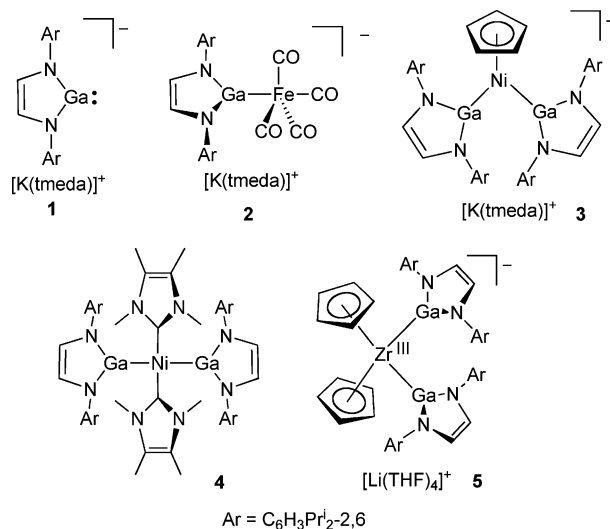
Centre for Fundamental and Applied Main Group Chemistry, School of Chemistry, Main Building, Cardiff University, Cardiff, UK CF10 3AT. E-mail: jonesca6@cardiff.ac.uk

† Electronic supplementary information (ESI) available: Cartesian coordinate files relating to the fully optimised geometries of compounds **6′**–**8′** and **9**–**11** together with atomic orbital contributions to important MOs in **6′**–**8′**. See DOI: 10.1039/b604640a


Ar = C$_6$H$_3$Pr$^i_2$-2,6

in situ generated "Cp$_2$Zr" fragment into the Ga–Ga bond of the digallane(4), [Ga{[N(Ar)C(H)]$_2$}]$_2$ (Ar = C$_6$H$_3$Pr$^i_2$-2,6), in the presence of Bu^{n}Li.[7] Although the exact mechanism of this reaction is unknown, the nature of the product highlights the ability of the gallium heterocycle to stabilise low oxidation state early transition metal fragments.

Considering the great importance of transition metal–NHC chemistry, and the fact that the coordination chemistry of related acyclic Group 13 metal(I) compounds (*e.g.* metal diyls, :M^{1}R, M = Al, Ga or In) has been widely studied,[8] it seemed appropriate to systematically extend the use of **1** as a ligand towards d-block metal fragments. In this paper we report on our efforts to form complexes of the gallium heterocycle with transition metal sandwich, half sandwich and dialkyl fragments. Comparisons with related NHC complexes are made where possible.

Results and discussion

(i)   Reactions with half sandwich complexes

In recent years a number of neutral or cationic half sandwich complexes of the type, [CpM(CO)$_n$(NHC)]$^{0 \text{ or } +1}$, have been reported and their use in catalysis has been suggested.[9] In attempts to form related neutral transition metal–gallyl complexes, either [CpFe(CO)$_2$I] or [CpMo(CO)$_3$Cl] were reacted with **1** in a 1 : 1 stoichiometry. The only isolated products of these reactions were, however, the paramagnetic gallium(II) dimers, [GaX{[N(Ar)C(H)˙]$_2$}]$_2$, X = I or Cl.[10] This suggests the reactions proceed *via* an initial insertion of the gallium(I) centre of **1** into the M–X bond of the transition metal complex, followed by decomposition of the formed intermediate. It is worth noting that gallium diyls, :GaR, and the neutral six-membered gallium heterocycle, [:Ga{[N(Ar)C(Me)]$_2$CH}], are now well known to insert into transition metal–halide bonds.[8,11] In order to circumvent this problem and to form related anionic complexes, **1** was reacted with a series of cyclopentadienyl–metal carbonyl half sandwich compounds which afforded the gallium heterocycle complexes, **6–8**, in moderate to good yields (Scheme 1). When the reactions were carried out in greater than 1 : 1 stoichiometries, only the 1 : 1 complexes resulted and the excess of **1** remained unreacted.
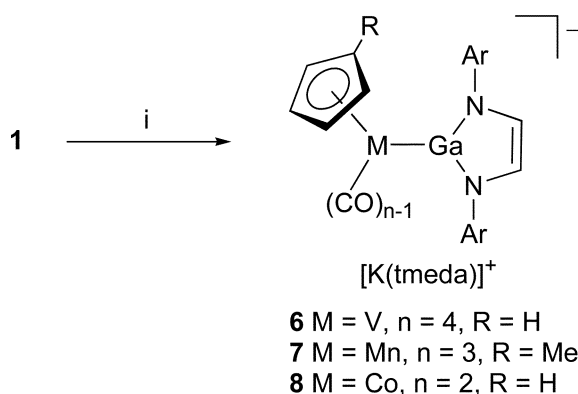
Scheme 1   i) (C$_5$H$_4$R)M(CO)$_n$, −CO.

Complexes **6–8** have been characterised by solution state multinuclear NMR (^{1}H, ^{13}C{^{1}H} and ^{51}V for **6**) and IR spectroscopy. The ^{1}H and ^{13}C{^{1}H} NMR spectra of all complexes are more

symmetrical than would be expected if their oligomeric/polymeric solid state structures (*vide infra*) were retained in solution. Therefore, it seems that in C$_6$D$_6$ solutions the associated forms of these compounds are not retained and there is free rotation of the gallium heterocycle about the M–Ga bonds. The ^{51}V NMR spectrum of **6** exhibits a signal at −1809 ppm ($\nu_{1/2}$ = 494 Hz) which is, not surprisingly, considerably upfield of the signal for the neutral starting material, [CpV(CO)$_4$] (−1533 ppm). It is also upfield of the resonance for the related anionic complex, [CpV(CO)$_3$H]$^-$ (−1730 ppm),[12] which might indicate that the gallium heterocycle is a better σ-donor than the hydride ligand.

The infrared spectra of **6–8** were acquired in THF/18-crown-6 solutions to minimise interactions between the cationic and anionic components of the complexes, as are seen in the solid state (*vide infra*). The positions of the CO stretching bands for these complexes (**6**: ν 1962, 1891, 1785 cm^{-1}; **7**: 1877, 1812 cm^{-1}; **8** 1690 cm^{-1}) are consistent with anionic complexes and that for **8** can be compared to the position of the band in the directly analogous neutral NHC complex, [CpCo(CO)(IPr)], IPr = :CN$_2$(Ar)$_2$C$_2$(H)$_2$ (ν 1921 cm^{-1}); for which less M–CO back bonding would be expected.[9d] A comparison of the CO stretching absorptions of **6** and **7** with those of the related hydride complexes, [CpM(CO)$_n$H]$^-$ (M = V, n = 3, ν CO = 1889, 1775 cm^{-1};[12] M = Mn, n = 2, ν CO = 1860, 1770 cm^{-1}[13]), shows that the latter appear at significantly lower wavenumbers which could indicate that the hydride ligand is a better σ-donor than the gallium heterocycle and/or that the gallium heterocycle has some π-acceptor capability. The first suggestion is at odds with our tentative assumption from the ^{51}V NMR spectrum of **6** that the gallium heterocycle is actually a better σ-donor than the hydride ligand.

X-Ray crystallographic studies were carried out on **6–8** and their molecular structures are depicted in Fig. 1–3 respectively. All three complexes are associated in the solid state. Complex **6** forms 1-dimensional polymeric strands *via* η^1-O-coordination of the potassium cation by two carbonyl ligands, chelation by a molecule of tmeda and an η^2-interaction with one arene substituent of the heterocycle. Both **7** and **8** form cyclic dimers, though that for **7** is held together with η^1-O-interactions from both carbonyl ligands of each monomeric unit to potassium centres, whilst the single carbonyl ligands of the monomeric units of **8** bridge the two K centres in an η^1-O:η^2-CO-fashion. The geometries of the coordinated gallium heterocycle in each complex are similar to each other and to the geometries in the majority of previously reported complexes of this heterocycle.[3–6] In addition, the least squares plane of the gallium heterocycle in each complex subtends a relatively acute angle with the Cp centroid–M–Ga containing plane (**6** 28.3° avge, **7** 28.1°, **8** 34.9°). This angle in **8** is significantly more acute than the related angle in its direct NHC analogue, [CpCo(CO)(IPr)] (45.9°).[9d] In addition, the angles in both **7** and **8** potentially allow the HOMO of the transition metal fragment[14] to overlap with the empty p-orbital at gallium, giving rise to π-bonding. An examination of the Cambridge Crystallographic Database revealed that complex **6** contains the first structurally authenticated V–Ga bond in a molecular compound. The Mn–Ga and Co–Ga bonds in **7** and **8** are shorter than any other examples of such bonds by more than 0.1 Å in each case (reported ranges Mn–Ga: 2.424–2.680 Å; Co–Ga: 2.342–2.708 Å[15]) and may also indicate M–Ga π-bonding. The shortness of these bonds is significant as previously reported examples of each
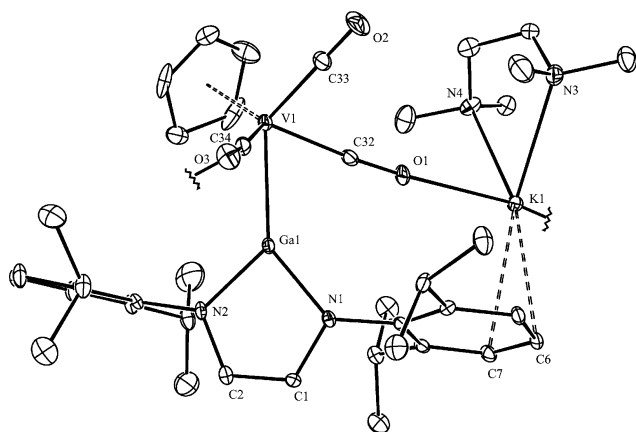
Fig. 1 Molecular structure of **6** (25% thermal ellipsoids are shown). Selected bond lengths (Å) and angles (°): Ga(1)–V(1) 2.4618(13), Ga(1)–N(1) 1.900(5), Ga(1)–N(2) 1.883(5), V(1)–C(32) 1.893(6), V(1)–C(33) 1.918(8), V(1)–C(34) 1.904(8), C(32)–O(1) 1.167(7), C(33)–O(2) 1.148(8), C(34)–O(3) 1.173(8), K(1)–O(1) 2.622(4), K(1)–N(4) 2.804(6), K(1)–N(3) 2.866(6), K(1)–C(6) 3.185(7), K(1)–C(7) 3.190(6), C(1)–N(1) 1.403(7), C(2)–N(2) 1.387(8), C(1)–C(2) 1.355(7); N(2)–Ga(1)–N(1) 86.9(2), N(2)–Ga(1)–V(1) 131.61(15), N(1)–Ga(1)–V(1) 141.47(14), C(32)–V(1)–C(34) 107.7(3), C(32)–V(1)–C(33) 79.6(3), C(34)–V(1)–C(33) 76.9(3), C(32)–V(1)–Ga(1) 67.96(19), C(34)–V(1)–Ga(1) 70.89(19), C(33)–V(1)–Ga(1) 123.2(3), N(4)–K(1)–N(3) 65.32(18), C(32)–O(1)–K(1) 173.0(5), O(1)–C(32)–V(1) 175.7(6), O(2)–C(33)–V(1) 178.4(8), O(3)–C(34)–V(1) 175.2(6).
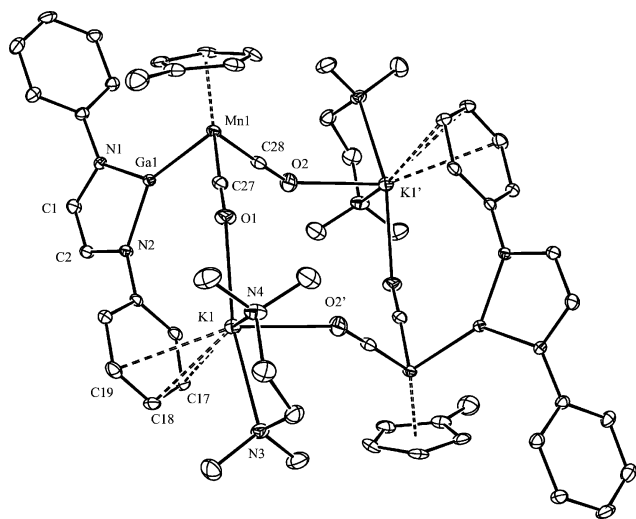

Fig. 2 Molecular structure of **7** (25% thermal ellipsoids are shown; isopropyl groups omitted for clarity). Selected bond lengths (Å) and angles (°): Ga(1)–N(1) 1.902(4), Ga(1)–N(2) 1.906(4), Ga(1)–Mn(1) 2.3105(9), Mn(1)–C(27) 1.749(6), Mn(1)–C(28) 1.752(6), K(1)–O(1) 2.627(4), K(1)–O(2)′ 2.663(4), K(1)–N(4) 2.840(5), K(1)–N(3) 2.855(4), K(1)–C(17) 3.187(5), K(1)–C(18) 3.102(5), K(1)–C(19) 3.193(5), O(1)–C(27) 1.174(6), O(2)–C(28) 1.175(6), O(2)–K(1)′ 2.663(4), N(1)–C(1) 1.388(6), N(2)–C(2) 1.400(6), C(1)–C(2) 1.339(7); N(1)–Ga(1)–N(2) 85.87(16), N(1)–Ga(1)–Mn(1) 133.78(12), N(2)–Ga(1)–Mn(1) 140.14(12), C(27)–Mn(1)–C(28) 92.5(3), C(27)–Mn(1)–Ga(1) 89.90(16), C(28)–Mn(1)–Ga(1) 85.80(17), O(1)–K(1)–O(2)′ 95.05(13), O(1)–K(1)–N(4) 78.40(13), N(4)–K(1)–N(3) 65.70(14), C(1)–N(1)–Ga(1) 110.8(3), C(2)–N(2)–Ga(1) 109.8(3), O(1)–C(27)–Mn(1) 176.5(5), O(2)–C(28)–Mn(1) 178.0(5). Symmetry transformations used to generate equivalent atoms: ′ $-x + 1/2$, $-y + 3/2$, $-z + 1/2$.
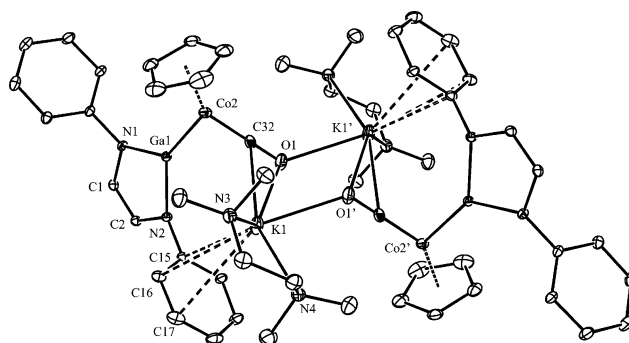

Fig. 3 Molecular structure of **8** (25% thermal ellipsoids are shown; isopropyl groups omitted for clarity). Selected bond lengths (Å) and angles (°): Ga(1)–N(1) 1.897(2), Ga(1)–N(2) 1.905(3), Ga(1)–Co(2) 2.2347(7), Co(2)–C(32) 1.677(4), K(1)–O(1)′ 2.758(3), K(1)–N(4) 2.899(3), K(1)–N(3) 2.954(3), K(1)–C(32) 3.121(4), K(1)–C(15) 3.669(3), K(1)–C(16) 3.609(4), K(1)–C(17) 3.698(4), O(1)–C(32) 1.186(5), N(1)–C(1) 1.400(4), N(2)–C(2) 1.397(4), C(1)–C(2) 1.339(4); N(1)–Ga(1)–N(2) 86.96(11), N(1)–Ga(1)–Co(2) 135.10(8), N(2)–Ga(1)–Co(2) 137.80(8), C(32)–Co(2)–Ga(1) 83.19(13), N(4)–K(1)–N(3) 61.20(9), O(1)′–K(1)–C(32) 75.24(10), O(1)′–K(1)–O(1) 60.92(10), C(32)–K(1)–O(1) 21.73(8), C(32)–O(1)–K(1)′ 128.8(3), K(1)′–O(1)–K(1) 119.08(10), C(1)–N(1)–Ga(1) 109.50(19), C(2)–N(2)–Ga(1) 109.2(2), O(1)–C(32)–Co(2) 178.2(4), O(1)–C(32)–K(1) 81.3(3). Symmetry transformations used to generate equivalent atoms: ′ $-x + 1$, $-y + 1$, $-z$.

include systems containing three-coordinate gallium centres, *e.g.* [Mes*Ga(Cl){Mn(CO)$_5$}] and [Mes*Ga{Co(CO)$_4$}$_2$], Mes* = C$_6$H$_2$Bu$^t_3$-2,4,6.[16]

In consideration of the very short M–Ga bonds, the orientation of the heterocycle planes in **7** and **8**, and the possibility that the positions of the CO stretching bands in the infrared spectra of **6–8** suggest M–Ga π-bonding in these compounds, it was decided to carry out DFT theoretical studies of models of these compounds using a well precedented computational approach.[17,18] Key results are listed in Table 1 for [CpV(CO)$_3${Ga{[N(Ph)C(H)]$_2$}]]$^-$ **6′**, [Cp′Mn(CO)$_2${Ga{[N(Ph)C(H)]$_2$}]]$^-$ **7′** (Cp′ = C$_5$H$_4$Me) and [CpCo-(CO){Ga{[N(Ph)C(H)]$_2$}]]$^-$ **8′**, which differ from the structurally characterised species **6–8** merely by replacement of the pendant Ar groups by the computationally less intensive Ph unit. Also included are the corresponding results for the valence isoelectronic (charge neutral) NHC complexes [CpV(CO)$_3${C{[N(Ph)C(H)]$_2$}]] **9**, [Cp′Mn(CO)$_2${C{[N(Ph)C(H)]$_2$}]] **10** and [CpCo(CO){C{[N(Ph)-C(H)]$_2$}]] **11**. Cartesian coordinate files relating to the fully optimised geometries of all six compounds (**6′**–**8′** and **9**–**11**) together with atomic orbital contributions to important MOs in **6′**–**8′** have been included in the ESI.†

In general, the agreement between calculated and experimentally observed molecular geometries is good, with the 2–3% overestimate in the lengths of the metal–metal bonds mirroring the results of previous studies.[17,18] Such phenomena have been ascribed to a combination of solid-state effects leading to the shortening of donor/acceptor bonds, and a general over-estimate of bond lengths by generalised gradient approximation (GGA) methods.[19] Moreover, previous studies have shown that little significant improvement in absolute agreement is achieved by the use of a higher level of theory (*e.g.* B3LYP rather than BLYP) or of the higher quality Gaussian basis set, 6-311++G(d) (B3LYP).[18] The generally good reproduction of the experimentally observed

Table 1 Calculated and measured structural and bonding parameters for compounds **6′–8′** and **9–11**

Compound	σ : π ratio	$r(Ga–M)^a$/Å	Angle between heterocycle and Cp centroid–M–Ga containing planes^a/°	Compound	σ : π ratio	$r(C–M)^a$/Å	Angle between heterocycle and Cp centroid–M–C containing planes^a/°
6′	87 : 13	2.554 [2.461(mean)]	33.3 [28.3]	**9**	86 : 14	2.315	36.7
7′	82 : 18	2.396 [2.311(1)]	29.4 [28.1]	**10**	79 : 21	2.061	27.3
8′	73 : 27	2.304 [2.235(1)]	41.5 [34.9]	**11**^{b}	74 : 26	1.918 [1.888(3)]	47.9 [45.9]

^{a} Calculated values given; experimental values in parentheses where applicable. ^{b} Experimental values for [CpCo(CO)(IPr)] taken from reference 9(d).

values for the angles between the gallium heterocycle and the Cp centroid–M–Ga containing least squares planes is reassuring, given that rotation around the metal–ligand axis in related systems has been shown to involve motion across a very shallow potential energy surface.[17]

The calculated σ : π ratios for **6′–8′** show the expected trend of increasing M → Ga π back-bonding on moving to more electron-rich late transition metal systems containing a decreasing number of competing π acidic carbonyl ligands. However, in each case the calculated π contribution is similar to that found for the corresponding valence isoelectronic NHC system, and similar in magnitude to values calculated for related half sandwich boryl complexes (ca. 10–20%).[18] NHC and boryl ligand systems have typically been described as strong σ-donor ligands with minor π acid capabilities.[20] Thus, the σ : π ratios for **6′–8′** can be put into the appropriate context by comparing them with the corresponding ratios of 86 : 14 and 66 : 33 for model systems containing formal M–Ga single and M=Ga double bonds, respectively.[17,21]

(ii) Reactions with sandwich complexes

The reactions of NHCs towards metallocenes have been studied in some detail. These normally lead to complexes of the type [Cp$_2$M(NHC)$_{1 or 2}$] in which the Cp ligands display varying degrees of "ring slippage", or to complete Cp anion displacement and the formation of cationic complexes, [CpM(NHC)$_2$][Cp].[22] These results prompted our earlier investigation into the reaction of **1** with nickelocene which similarly yielded **3**.[6] Subsequently we have investigated the reaction of **1** with a range of first row metallocenes which either led to no reaction (with FeCp$_2$), to intractable mixtures of products (with MCp$_2$, M = V, Cr or Mn) or in the reaction with cobaltocene, the cobalt analogue of **3**.[3]

Considering the limited success had with these reactions it was decided to attempt the formation of neutral metallocene–gallyl complexes via the oxidative insertion of metallocenes into the Ga–Ga bond of the digallane(4), [Ga{[N(Ar)C(H)]$_2$}]$_2$, **12**. This work is directly related to the formation of **5**, and has precedent in boryl chemistry with the reaction of "Cp$_2$W" with B$_2$Cat′$_2$, Cat′ = 4-Bu^{t}C$_6$H$_3$O$_2$-1,2 or 3,5-Bu$^t_2$C$_6$H$_2$O$_2$-1,2, which gave the bis-boryl complexes [Cp$_2$W(BCat′)$_2$].[23] Although a synthetic route to the digallane, **12**, has been reported,[24] we have previously commented that the same compound can be prepared in high yield by oxidatively coupling the gallium(I) heterocycle of **1** in its treatment with the ferrocenium cation.[4d] Full details of this synthetic procedure are included here.

The 1 : 1 reactions of the metallocenes Cp′$_2$M (M = V or Cr) with **12** afforded the neutral mono-gallyl complexes, [Cp′$_2$M[Ga{[N(Ar)C(H)]$_2$}]] (M = V **13**, Cr **14**) in low yield
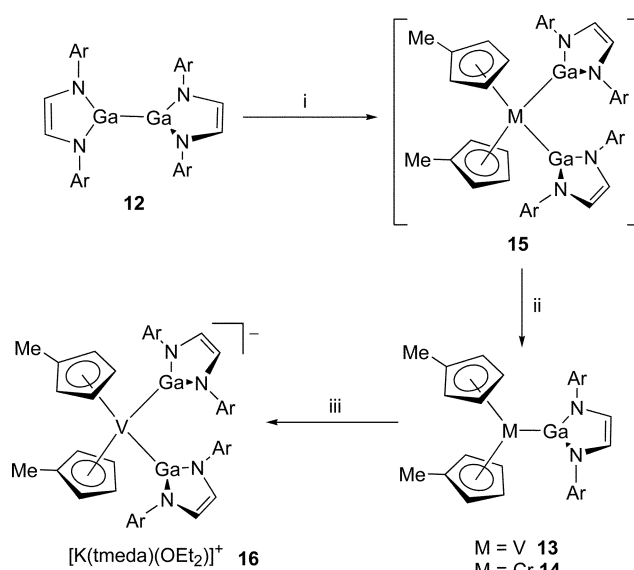
Scheme 2 i) M(Cp′)$_2$, OEt$_2$; ii) M(Cp′)$_2$; iii) M = V, **1**, OEt$_2$.

(<10%) after work-up (Scheme 2). Presumably, the mechanisms of these reactions involve an initial oxidative insertion of the transition metal centre into the Ga–Ga bond of **12** to give the bis-gallyl complexes, **15**, which then undergo comproportionation reactions with Cp′$_2$M to give the observed products. In line with this hypothesis is the fact that when the reactions were repeated in a 1 : 0.5 stoichiometry, complexes **13** and **14** were obtained in moderate to good yields. Attempts to extend this chemistry to other transition metals by reacting **12** with Cp′$_2$Mn, Cp$_2$Ti(CO)$_2$ or "Cp$_2$W" (generated from Cp$_2$WH$_2$ under UV conditions) all afforded intractable mixtures of products. We have previously shown that treating **3** with an NHC led to Cp anion displacement and the formation of **4**.[6] When **13** or **14** were treated with the same NHC in this study, no reaction occurred. Interestingly, when these complexes were treated with the gallium NHC analogue, **1**, a reaction occurred with **13** to give the anionic complex **16** (Scheme 2), but no reaction was observed with **14**. Perhaps the reason for this difference lies with the larger covalent radius of vanadium relative to chromium and the fact that the chromium analogue of **16** would be a 19-electron species. It is of note that complex **16** is closely related to the zirconium complex, **5**.

Given the paramagnetic nature of **13** and **14**, meaningful NMR spectroscopic data could not be obtained for these complexes. As a result, all were crystallographically characterised. Compounds **13** and **14** were found to be isomorphous and therefore only the ORTEP diagram for **13** is depicted in Fig. 4. The Ga–V bond length of **13** is significantly longer than that in anionic **6**,
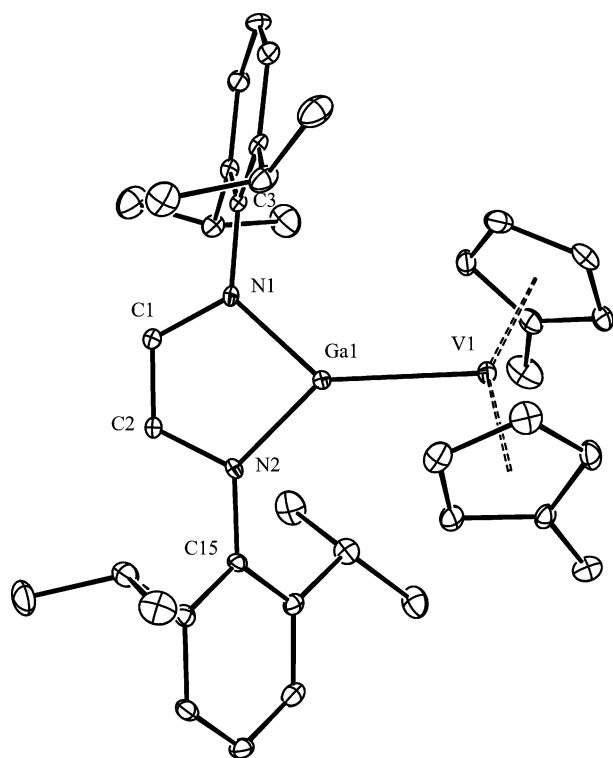
Fig. 4 Molecular structure of **13** (25% thermal ellipsoids are shown). Selected bond lengths (Å) and angles (°): Ga(1)–N(1) 1.899(3), Ga(1)–N(2) 1.901(3), Ga(1)–V(1) 2.5303(9), N(1)–C(1) 1.389(5), N(2)–C(2) 1.404(5), C(1)–C(2) 1.344(5); N(1)–Ga(1)–N(2) 86.39(14), N(1)–Ga(1)–V(1) 135.78(10), N(2)–Ga(1)–V(1) 137.74(10), C(1)–N(1)–Ga(1) 110.6(3), C(2)–N(2)–Ga(1) 109.6(3). Selected bond lengths (Å) and angles (°) for isomorphous **14**: Ga(1)–N(2) 1.901(4), Ga(1)–N(1) 1.894(4), Ga(1)–Cr(1) 2.4231(11), N(2)–C(2) 1.406(6), N(1)–C(1) 1.391(7), C(1)–C(2) 1.355(7); N(2)–Ga(1)–N(1) 86.81(17), N(2)–Ga(1)–Cr(1) 137.58(13), N(1)–Ga(1)–Cr(1) 135.46(13), C(1)–N(1)–Ga(1) 110.7(3), C(2)–N(2)–Ga(1) 109.3(3).

whilst the Cr–Ga distance in **14** lies within the known range for such interactions (2.390–2.479 Å).[15] Both complexes are bent with centroid–M–centroid angles of 148.8°, **13**, and 151.4°, **14**, and the heterocyclic planes intersect the centroid–M–centroid–Ga least squares planes by 37.6°, **13**, and 40.8°, **14**. The geometries of the coordinated Ga heterocycles are similar to those in **6–8**. In the structure of **16** (Fig. 5) the anion and cation are associated through interactions between the potassium centre and one Cp′ and one heterocycle Ar substituent. Surprisingly, the Ga–V distances in this compound are slightly shorter than in the presumably less crowded neutral complex, **13**. Comparisons can also be made with the structural parameters of the related zirconium complex, **5**, most notably the Ga–M–Ga (**16**: 82.59(5)°; **5** 87.70(3)°) and centroid–M–centroid angles (**16**: 140.0°; **5**: 136.1°) of both complexes.

(iii) Reactions with dialkylmanganese complexes

As little success was had in the reactions of **1** or **12** with manganocenes, the two gallium compounds were treated with the manganese dialkyls, [Mn{C(SiMe₃)₃}₂] and [Mn{CH(SiMe₃)₂}₂]. No reactions were observed with the bulkier dialkyl complex and similarly no reaction occurred between [Mn{CH(SiMe₃)₂}₂] and the digallane, **12**. In contrast, the reaction between [Mn{CH(SiMe₃)₂}₂] and **1** afforded the anionic complex, **17**,
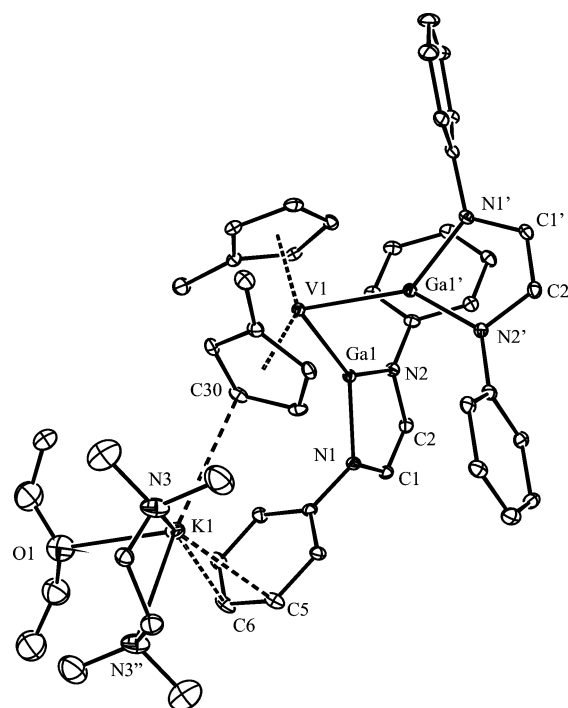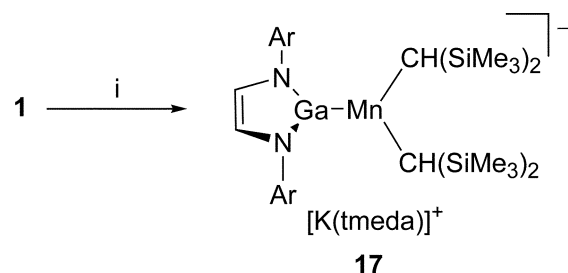

Fig. 5 Molecular structure of **16** (25% thermal ellipsoids are shown; isopropyl groups omitted for clarity). Selected bond lengths (Å) and angles (°): Ga(1)–N(2) 1.930(4), Ga(1)–N(1) 1.966(5), Ga(1)–V(1) 2.5093(12), K(1)–O(1) 2.907(15), K(1)–N(3) 2.965(9), K(1)–N(3)′ 3.082(9), K(1)–C(30) 3.248(7), K(1)–C(5) 3.022(8), K(1)–C(6) 3.061(8), N(1)–C(1) 1.398(7), N(2)–C(2) 1.396(7), C(1)–C(2) 1.330(8); N(2)–Ga(1)–N(1) 84.9(2), N(2)–Ga(1)–V(1) 141.30(14), N(1)–Ga(1)–V(1) 133.64(14), Ga(1)′–V(1)–Ga(1) 82.59(5), N(3)–K(1)–N(3)′ 58.8(2), C(1)–N(1)–Ga(1) 109.0(4), C(2)–N(2)–Ga(1) 110.5(4). Symmetry transformations used to generate equivalent atoms: ′ −x + 1, y, −z + 1/2; ″ −x + 1, −y, −z.

in moderate yield (Scheme 3). The complex is related to other adducts of manganese dialkyls, most notably the three coordinate monomeric complex, [Mn{CH(SiMe₃)₂}₂(THF)].[25] The paramagnetic nature of **17** meant that little meaningful NMR data could be obtained on this compound. Although the magnetic moment of **17** in solution is lower than expected for a high spin d^5 complex ($\mu_{eff} = 4.62\,\mu_B$ by the Evans' method), it is in the range previously observed for high spin complexes of manganese(II) alkyls.[25]

Scheme 3 i) Mn{CH(SiMe₃)₂}₂, OEt₂.

The molecular structure of **17** is depicted in Fig. 6. This shows it to be monomeric with a three-coordinate distorted trigonal planar manganese centre. The anionic gallium heterocycle has an η⁵-interaction with the potassium counter-ion which is additionally chelated by a molecule of tmeda. The structure of this
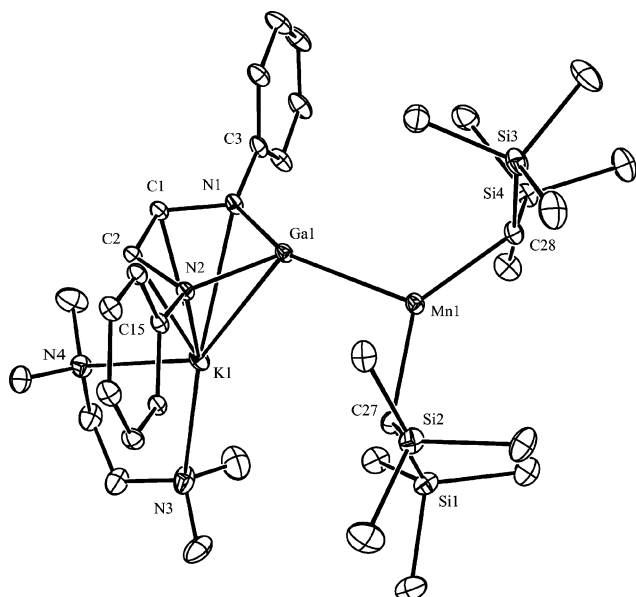
Fig. 6 Molecular structure of **17** (25% thermal ellipsoids are shown; isopropyl groups omitted for clarity). Selected bond lengths (Å) and angles (°): Ga(1)–N(1) 1.940(3), Ga(1)–N(2) 1.946(3), Ga(1)–Mn(1) 2.6658(10), Ga(1)–K(1) 3.4925(15), Mn(1)–C(28) 2.143(4), Mn(1)–C(27) 2.158(5), K(1)–N(4) 2.839(4), K(1)–N(3) 2.863(5), K(1)–C(2) 3.052(4), K(1)–C(1) 3.081(5), K(1)–N(2) 3.093(4), K(1)–N(1) 3.150(4); N(1)–Ga(1)–N(2) 84.16(14), N(1)–Ga(1)–Mn(1) 147.69(11), N(2)–Ga(1)–Mn(1) 125.93(10), C(28)–Mn(1)–C(27) 134.12(18), C(28)–Mn(1)–Ga(1) 122.97(14), C(27)–Mn(1)–Ga(1) 102.88(12).

heterocycle–potassium ion pair is very similar to that seen in **1** itself,[2] though in that compound two such ion pairs form a dimer through two intermolecular Ga lone pair–K interactions. It is of interest that the Ga–Mn distance in **17** is more than 0.3 Å longer than that in the half sandwich complex, **7**. Despite this, it lies in the normal range.[15] In addition, it can be surmised that the gallium heterocycle is a significantly stronger σ-donor than THF as the C–Mn–C angle in **17** is more than 25° narrower than in the related adduct, [Mn{CH(SiMe$_3$)$_2$}$_2$(THF)] 160.1(9)°.[25] Finally, the gallium heterocycle is not co-planar with the manganese dialkyl fragment and forms an angle of 28.3° with the least squares plane containing the C$_2$MnGa fragment.

Conclusion

In summary, several anionic complexes of a gallium(I) hetero-cycle, [Ga{[N(Ar)C(H)]$_2$}]$^-$, with transition metal half sandwich fragments have been prepared by reaction of the heterocycle with suitable metal precursors. Although there is crystallographic and some spectroscopic evidence to suggest the possibility of significant M–Ga π-bonding in these species, a theoretical study on models of these compounds suggests they exhibit no more back-bonding than do analogous neutral NHC complexes. A range of complexes of the gallium heterocycle with transition metal sandwich fragments and a manganese dialkyl have also been prepared by reactions of the metal dialkyls with a digallane(4), [Ga{[N(Ar)C(H)]$_2$}]$_2$, or the anionic gallium(I) heterocycle. The prepared complexes display M–Ga bond lengths that are not suggestive of any π-bonding. This study further highlights the

similarities between the anionic gallium heterocycle and valence isoelectronic NHCs.

Experimental

General considerations

All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of high purity argon. THF and hexane were distilled over potassium whilst diethyl ether was distilled over Na/K alloy. Melting points were determined in sealed glass capillaries under argon and are uncorrected. Mass spectra were recorded using a VG Fisons Platform II instrument under APCI conditions or were obtained from the EPSRC National Mass Spectrometric Service at Swansea University. Microanalyses were obtained from Medac Ltd. IR spectra were recorded using a Nicolet 510 FT-IR spectrometer as Nujol mulls between NaCl plates. ^{1}H and ^{13}C NMR spectra were recorded on either a Bruker DXP400 spectrometer operating at 400.13 and 100 MHz respectively, or a Jeol Eclipse 300 spectrometer operating at 300.52 and 75.57 MHz respectively and were referenced to the resonances of the solvent used. The ^{51}V NMR spectrum was recorded on a Jeol Eclipse 300 spectrometer operating at 78.91 MHz and referenced relative to external VOCl$_3$ ($\delta = 0$ ppm). The magnetic moment determination was carried out using the Evans' method.[26] The compounds [K(tmeda)][Ga{[N(Ar)C(H)]$_2$}][2] and [Mn{CH(SiMe$_3$)$_2$}$_2$][27] were synthesized according to literature procedures, whilst all other reactants were obtained commercially and used as received.

Syntheses

Preparation of [K(tmeda)][CpV(CO)$_3$[Ga{[N(Ar)C(H)]$_2$}]] 6. To a solution of [K(tmeda)][:Ga{[N(Ar)C(H)]$_2$}] (0.30 g, 0.50 mmol) in THF (15 cm^3) was added a solution of [CpV(CO)$_4$] (0.11 g, 0.50 mmol) in THF (15 cm^3) at −78 °C over 5 minutes. The resultant yellow solution was warmed to room temperature and stirred overnight. Volatiles were removed *in vacuo* and the residue extracted with hexane (20 cm^3). Filtration, concentration and cooling to −30 °C overnight yielded yellow/orange crystals of **6** (0.22 g, 54%). Mp 164–166 °C; ^{1}H NMR (400 MHz, C$_6$D$_6$, 298 K): $\delta = 0.96$ (d, $^3J_{HH} = 6.8$ Hz, 12H, CH(CH$_3$)$_2$), 0.99 (d, $^3J_{HH} = 6.8$ Hz, 12H, CH(CH$_3$)$_2$), 1.75 (s, 12H, NCH$_3$), 1.94 (s, 4H, NCH$_2$), 3.80 (v. sept, $^3J_{HH} = 6.8$ Hz, 4H, CH(CH$_3$)$_2$), 4.51 (s, 5H, CpH), 6.26 (s, 2H, NC$_2$H$_2$N), 6.71 (t, $^3J_{HH} = 7.7$ Hz, 2H, p-ArH), 8.89 (d, $^3J_{HH} = 7.7$ Hz, 4H, m-ArH); ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$, 298 K): $\delta = 23.7$ (CH(CH$_3$)$_2$), 24.1 (CH(CH$_3$)$_2$), 25.9 (CH(CH$_3$)$_2$), 45.0 (NCH$_3$), 56.8 (NCH$_2$), 87.6 (Cp), 117.0 (N$_2$C$_2$H$_2$), 122.9 (m-ArC), 123.7 (p-ArC), 147.2 (o-ArC), 148.7 (ipso-ArC), CO resonance not observed; ^{51}V NMR (79 MHz, C$_6$D$_6$, 298 K): $\delta = -1809$ ppm (s); IR ν/cm^{-1} (THF/18-crown-6): 1962(s), 1891(s), 1785(br.s); m/z (CI/−ve): 645.2 [[CpV(CO)$_3$[Ga{[N(Ar)C(H)]$_2$}]]$^-$, 40%], 617.0 [[CpV(CO)$_2$[Ga{[N(Ar)C(H)]$_2$}]]$^-$, 55%], 376 [{N(Ar)C(H)}$_2$$^-$, 100%]; Acc. mass (CI/−ve): calc. for C$_{34}$H$_{41}$O$_3$N$_2$^{69}Ga^{51}V: 645.1818; obsvd. 645.1816.

Preparation of [K(tmeda)][Cp′Mn(CO)$_2$[Ga{[N(Ar)C(H)]$_2$}]] 7. To a solution of [K(tmeda)][:Ga{[N(Ar)C(H)]$_2$}] (0.20 g, 0.34 mmol) in THF (15 cm^3) was added a solution of [Cp′Mn(CO)$_3$] (0.07 g, 0.33 mmol) in THF (35 cm^3). The mixture

was irradiated with a UV lamp for 2 hours at $-78\,^\circ$C. The resultant solution was warmed to room temperature and stirred overnight to yield a yellow solution. Volatiles were removed *in vacuo* and the residue extracted with hexane (20 cm³). Filtration, concentration and cooling to $-30\,^\circ$C overnight yielded yellow/orange crystals of **7** (0.12 g, 46%). Mp 255–257 °C; ¹H NMR (300 MHz, C_6D_6, 298 K): $\delta = 1.11$ (d, 12H, $^3J_{HH} = 6.6$ Hz, CH(CH_3)$_2$), 1.15 (d, 12H, $^3J_{HH} = 6.6$ Hz, CH(CH_3)$_2$), 1.51 (s, 3H, C_5H_4(CH)), 1.82 (s, 12H, NCH$_3$), 1.96 (s, 4H, NCH$_2$), 3.15 (v. sept, $^3J_{HH} = 6.6$ Hz, 4H, CH(CH$_3$)$_2$), 3.87 (m, 2H, CpH), 4.06 (m, 2H, Cp), 6.24 (s, 2H, N$_2C_2H_2$), 6.80–7.20 (m, 6H, ArH); ¹³C{¹H} NMR (75 MHz, C_6D_6, 298 K): $\delta = 23.4$ (C_5H_4(CH$_3$)), 23.8 (CH(CH$_3$)$_2$), 25.9 (CH(CH$_3$)$_2$), 28.4 (CH(CH$_3$)$_2$), 44.8 (NCH$_3$), 56.7 (NCH$_2$), 76.7, 78.9, 96.8 (Cp), 122.3 (NC_2H_2), 122.8 (*m*-ArC), 123.7 (*p*-ArC), 147.7 (*o*-ArC), 150.4 (*ipso*-ArC), 238.3 (CO); IR ν/cm⁻¹ (THF/18-crown-6): 1877(s), 1812(s); *m/z* (APCI): 377 [{N(Ar)C(H)}$_2$H⁺, 100%].

Preparation of [K(tmeda)][CpCo(CO){Ga{[N(Ar)C(H)]$_2$}]] 8. To a solution of [K(tmeda)][:Ga{[N(Ar)C(H)]$_2$}] (0.30 g, 0.50 mmol) in diethyl ether (15 cm³) was added a solution of [CpCo(CO)$_2$] (0.09 g, 0.50 mmol) in diethyl ether (15 cm³) at $-78\,^\circ$C over 5 minutes. The resultant solution was warmed to room temperature and stirred overnight to yield a red solution. Volatiles were removed *in vacuo* and the residue extracted with hexane (20 cm³). Filtration, concentration and cooling to $-30\,^\circ$C overnight yielded red crystals of **8** (0.26 g, 66%). Mp 118–120 °C; ¹H NMR (250 MHz, C_6D_6, 298 K): $\delta = 1.49$ (v. t, $^3J_{HH} = 6.6$ Hz, 24H, CH(CH_3)$_2$), 1.89 (s, 12H, NCH$_3$), 2.03 (s, 4H, NCH$_2$), 3.77 (v. sept, $^3J_{HH} = 6.6$ Hz, 4H, CH(CH$_3$)$_2$), 4.40 (s, 5H, CpH), 6.18 (s, 2H, N$_2C_2H_2$), 6.90–7.26 (m, 6H, ArH); ¹³C{¹H} NMR (75 MHz, C_6D_6, 298 K): $\delta = 24.2$ (CH(CH$_3$)$_2$), 25.2 (CH(CH$_3$)$_2$), 28.0 (CH(CH$_3$)$_2$), 45.2 (NCH$_3$), 57.1 (NCH$_2$), 77.1 (Cp), 121.8 (N$_2C_2H_2$), 122.7 (*m*-ArC), 123.7 (*p*-ArC), 147.2 (*o*-ArC), 149.2 (*ipso*-Ar), 209.1 (CO); IR ν/cm⁻¹ (THF/18-crown-6): 1690(s); *m/z* (APCI): 377 [{N(Ar)C(H)}$_2$H⁺, 75%].

To a suspension of [(Cp)$_2$Fe][PF$_6$] (0.32 g, 1.0 mmol) in diethyl ether (10 cm³) was added a solution of **1** (0.50 g, 0.82 mmol) in diethyl ether (30 cm³) and the mixture stirred for 6 h. Volatiles were removed *in vacuo* and the ferrocene product sublimed from the residue (25 °C, 0.1 mmHg). The resultant red powder was recrystallised from hexane at $-30\,^\circ$C to yield deep red **12** (0.31 g, 87%). The spectroscopic data for this compound were identical to those previously reported.[24]

Preparation of [(Cp′)$_2$V[Ga{[N(Ar)C(H)]$_2$}]] 13. To a solution of V(Cp′)$_2$ (0.12 g, 0.57 mmol) in diethyl ether (20 cm³) was added a solution of **12** (0.25 g, 0.28 mmol) in diethyl ether (20 cm³) at $-78\,^\circ$C. The mixture was allowed to warm to room temperature and stirred for 12 h. Volatiles were removed *in vacuo* and the residue extracted with hexane (20 cm³). Concentration and placement at $-35\,^\circ$C overnight yielded red crystals of **13** (0.24 g, 63%). Mp 148–153 °C (decomp.); IR (Nujol) ν/cm⁻¹: 1619(m), 1459(s), 1260(s), 1094(s), 865(m); *m/z* (APCI): 377 [{N(Ar)C(H)}$_2$H⁺, 100%], 209 [Cp′$_2$V⁺, 51%]; $C_{38}H_{50}N_2GaV$ requires: C 69.63%, H 7.69%, N 4.27%; found: C 68.71%, H 7.56%, N 4.40%.

Preparation of [(Cp′)$_2$Cr[Ga{[N(Ar)C(H)]$_2$}]] 14. To a solution of Cr(Cp′)$_2$ (0.12 g, 0.57 mmol) in diethyl ether (20 cm³) was added a solution of **12** (0.25 g, 0.28 mmol) in diethyl ether (20 cm³) at $-78\,^\circ$C. The mixture was allowed to warm to room temperature

Table 2 Crystal data for compounds 6–8, 13, 14, 16 and 17·hexane

Compound	6	7	8	13	14	16	17·hexane
Empirical formula	$C_{40}H_{57}GaKN_4O_3V$	$C_{40}H_{59}GaK\ MnN_4O_2$	$C_{38}H_{57}GaKCoN_4O$	$C_{38}H_{50}GaN_2V$	$C_{38}H_{50}GaN_2Cr$	$C_{74}H_{112}Ga_2KN_6OV$	$C_{52}H_{104}GaKMnN_4Si_4$
M	801.66	791.67	753.63	655.46	656.52	1331.18	1061.51
T/K	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
Crystal system	Orthorhombic	Tetragonal	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$Pca2_1$	$I4_1/a$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$C2/c$	$P\bar{1}$
a/Å	31.855(6)	37.980(5)	11.860(2)	13.340(3)	13.338(3)	22.944(5)	12.697(3)
b/Å	10.205(2)	37.980(5)	14.192(3)	16.734(3)	16.529(3)	12.436(3)	14.656(3)
c/Å	25.904(5)	13.689(3)	23.631(5)	15.496(3)	15.433(3)	27.243(5)	17.878(4)
α/°	90	90	90	90	90	90	108.31(3)
β/°	90	90	96.05(3)	93.39(3)	91.67(3)	98.47(3)	96.90(3)
γ/°	90	90	90	90	90	90	92.94(3)
V/Å³	8421(3)	19746(6)	3955.3(14)	3453.1(12)	3401.0(12)	7689(3)	3121.5(11)
Z	8	16	4	4	4	4	2
D_{calc}/Mg m⁻³	1.265	1.065	1.266	1.261	1.282	1.150	1.129
μ(Mo-K$_\alpha$)/mm⁻¹	1.000	0.916	1.238	1.078	1.139	0.912	0.811
F(000)	3376	6688	1592	1384	1388	2840	1150
No. of reflections collected	48240	47391	21460	18418	22448	12562	20196
No. of independent reflns (R_{int})	15263 (0.1080)	8667 (0.1052)	7999 (0.0609)	6267 (0.0941)	5978 (0.1574)	6726 (0.0413)	10864 (0.0335)
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0607$ $wR2 = 0.1140$	$R1 = 0.0709$ $wR2 = 0.1606$	$R1 = 0.0509$ $wR2 = 0.0946$	$R1 = 0.0588$ $wR2 = 0.1184$	$R1 = 0.0696$ $wR2 = 0.1369$	$R1 = 0.0736$ $wR2 = 0.1903$	$R1 = 0.0709$ $wR2 = 0.1914$

and stirred for 12 h. Volatiles were removed *in vacuo* and the residue extracted with hexane (20 cm³). Concentration and placement at −35 °C overnight yielded red crystals of **14** (0.30 g, 78%). Mp 186–189 °C (decomp.); IR (Nujol) *v*/cm⁻¹: 1619(m), 1459(s), 1317(m), 1260(s), 1021(m), 865(m); *m/z* (APCI): 377 [{N(Ar)C(H)}₂H⁺, 100%]; C₃₈H₅₀N₂GaCr requires: C 69.52%, H 7.68%, N 4.26%; found: C 68.89%, H 7.49%, N 4.17%.

Preparation of [K(tmeda)(OEt₂)][(Cp′)₂V[Ga{[N(Ar)C(H)]₂}]₂] 16. To a solution of **13** (0.24 g, 0.36 mmol) in diethyl ether (20 cm³) held at −78 °C was added a solution of **1** (0.23 g, 0.38 mmol) in diethyl ether (20 cm³). The mixture was allowed to warm to room temperature and stirred overnight. Volatiles were removed *in vacuo* and the residue washed with hexane (2 × 20 cm³) and then extracted into diethyl ether (50 cm³). Concentration and placement at −35 °C overnight yielded red crystals of **16** (0.28 g, 58%). Mp 82–86 °C(decomp.); IR (Nujol) *v*/cm⁻¹: 1589 (m), 1459 (s), 1260 (s), 1100 (s), 802 (s); *m/z* (APCI): 377 [{N(Ar)C(H)}₂H⁺, 100%]; C₇₄H₁₁₂N₆Ga₂VOK requires: C 66.77%, H 8.48%, N 6.31%; found: C 65.99%, H 8.29%, N 6.17%.

Preparation of [K(tmeda)][Mn{CH(SiMe₃)₂}₂[Ga{[N(Ar)C(H)]₂}]] 17. [K(tmeda)][:Ga{[N(Ar)C(H)]₂}] (0.41 g, 0.68 mmol) in diethyl ether (25 cm³) was added to a solution of [Mn{CH(SiMe₃)₂}₂] (0.26 g, 0.68 mmol) in diethyl ether (25 cm³) at −78 °C over 15 min. The resultant red solution was warmed to room temperature over 1 hour and stirred overnight. Volatiles were removed *in vacuo* and the residue extracted with hexane (20 cm³). Filtration, concentration and cooling to −30 °C overnight yielded red crystals of **17** (0.30 g, 45%). Mp = 85–87 °C; IR *v*/cm⁻¹ (Nujol): 1854(s), 1251(s), 1091(s), 1033(s), 851(s); *m/z* (APCI): 377 [{N(Ar)C(H)}₂H⁺, 100%]; μ_{eff} = 4.62 μ_B; C₄₆H₉₀N₄GaKMnSi₄ requires: C 56.65%, H 9.30%, N 5.74%; found: C 56.51%, H 8.96%, N 5.58%.

X-Ray crystallography

Crystals of **6–8**, **13**, **14**, **16** and **17** suitable for X-ray structural determination were mounted in silicone oil. Crystallographic measurements were made using a Nonius Kappa CCD diffractometer. The structures were solved by direct methods and refined on F^2 by full matrix least squares (SHELX97)[28] using all unique data. All non-hydrogen atoms are anisotropic with H-atoms included in calculated positions (riding model). Crystal data, details of data collections and refinement are given in Table 2.

CCDC reference numbers 603226–603232.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b604640a

References

1 See for example: (*a*) N. Kuhn and A. Al-Sheikh, *Coord. Chem. Rev.*, 2005, **249**, 829; (*b*) W. Kirmse, *Eur. J. Org. Chem.*, 2005, 237; (*c*) W. A. Herrmann, *Angew. Chem., Int. Ed.*, 2002, **41**, 1291; (*d*) C. J. Carmalt and A. H. Cowley, *Adv. Inorg. Chem.*, 2000, **50**, 1; (*e*) D. Bourissou, O. Guerret, F. P. Gabai and G. Bertrand, *Chem. Rev.*, 2000, **100**, 39 and references therein.
2 R. J. Baker, R. D. Farley, C. Jones, M. Kloth and D. M. Murphy, *J. Chem. Soc., Dalton Trans.*, 2002, 3844. NB: A synthesis of a related anion, [:Ga{[N(Buᵗ)C(H)]₂}]⁻, has been previously reported, see: E. S. Schmidt, A. Jockisch and H. Schmidbaur, *J. Am. Chem. Soc.*, 1999, **121**, 9358.
3 R. J. Baker and C. Jones, *Coord. Chem. Rev.*, 2005, **149**, 1857 and references therein.
4 (*a*) C. Jones, D. P. Mills, J. A. Platts and R. P. Rose, *Inorg. Chem.*, 2006, **45**, 3146; (*b*) R. J. Baker, C. Jones, D. P. Mills, D. M. Murphy, E. Hey-Hawkins and R. Wolf, *Dalton Trans.*, 2006, 64; (*c*) R. J. Baker, C. Jones and M. Kloth, *Dalton Trans.*, 2005, 2106; (*d*) R. J. Baker, C. Jones, M. Kloth and J. A. Platts, *Organometallics*, 2004, **23**, 4811; (*e*) R. J. Baker, C. Jones, M. Kloth and J. A. Platts, *Angew. Chem., Int. Ed.*, 2003, **43**, 2660.
5 R. J. Baker, C. Jones and J. A. Platts, *Dalton Trans.*, 2003, 3673.
6 R. J. Baker, C. Jones and J. A. Platts, *J. Am. Chem. Soc.*, 2003, **125**, 10534.
7 R. J. Baker, C. Jones and D. M. Murphy, *Chem. Commun.*, 2005, 1339.
8 See for example: (*a*) X.-J. Yang, Y. Wang, B. Quillian, P. Wei, Z. Chen, P. v. R. Schleyer and G. H. Robinson, *Organometallics*, 2006, **25**, 925; (*b*) G. Gemel, T. Steinke, M. Cokoja, A. Kempter and R. A. Fischer, *Eur. J. Inorg. Chem.*, 2004, 4161 and references therein.
9 See for example: (*a*) E. Fooladi, B. Dalhus and M. Tilset, *Dalton Trans.*, 2004, 3909; (*b*) P. Buchgraber, L. Toupet and V. Guerchais, *Organometallics*, 2003, **22**, 5144; (*c*) V. K. Dioumaev, D. J. Szalda, J. Hanson, J. A. Franz and R. M. Bullock, *Chem. Commun.*, 2003, 1670; (*d*) R. W. Simms, M. J. Drewitt and M. C. Baird, *Organometallics*, 2002, **21**, 2958.
10 R. J. Baker, R. D. Farley, C. Jones, D. P. Mills, M. Kloth and D. M. Murphy, *Chem. Eur. J.*, 2005, **11**, 2972.
11 A. Kempter, C. Gemel, N. J. Hardman and R. A. Fischer, *Inorg. Chem.*, 2006, **45**, 3133.
12 U. Puttfarcken and D. Rehder, *J. Organomet. Chem.*, 1980, **185**, 219.
13 V. S. Leong and N. J. Cooper, *Organometallics*, 1988, **7**, 2080.
14 (*a*) B. E. R. Schilling, R. Hoffmann and D. Lichtenberger, *J. Am. Chem. Soc.*, 1979, **101**, 585; (*b*) P. Hoffman and M. Padmanabhan, *Organometallics*, 1983, **2**, 1273.
15 As determined by a survey of the Cambridge Crystallographic Database, April, 2006.
16 A. H. Cowley, A. Decken, C. A. Olazabal and N. C. Norman, *Inorg. Chem.*, 1994, **33**, 3435.
17 S. Aldridge, A. Rossin, D. L. Coombs and D. J. Willock, *Dalton Trans.*, 2004, 2649.
18 A. A. Dickinson, D. J. Willock, R. J. Calder and S. Aldridge, *Organometallics*, 2001, **21**, 1146.
19 See for example: (*a*) E. A. McCullough, Jr., E. Aprà and J. Nichols, *J. Phys. Chem. A*, 1997, **101**, 2502; (*b*) C. L. B. Macdonald and A. H. Cowley, *J. Am. Chem. Soc.*, 1999, **121**, 12113; (*c*) J. Uddin, C. Boehme and G. Frenking, *Organometallics*, 2000, **19**, 571; (*d*) J. Uddin and G. Frenking, *J. Am. Chem. Soc.*, 2001, **123**, 1683.
20 J. Zhu, Z. Lin and T. B. Marder, *Inorg. Chem.*, 2005, **44**, 9384.
21 N. R. Bunn, S. Aldridge, D. L. Coombs, A. Rossin, D. J. Willock, C. Jones and L.-L. Ooi, *Chem. Commun.*, 2004, 1732.
22 (*a*) C. D. Abernethy, A. H. Cowley, R. A. Jones, C. L. B. Macdonald, P. Shukla and L. K. Thompson, *Organometallics*, 2001, **20**, 3629; (*b*) C. D. Abernethy, J. A. C. Clyburne, A. H. Cowley and R. A. Jones, *J. Am. Chem. Soc.*, 1999, **121**, 2329.
23 J. F. Hartwig and X. He, *Organometallics*, 1996, **15**, 5350.
24 T. Pott, P. Jutzi, W. W. Schoeller, A. Stammler and H.-G. Stammler, *Organometallics*, 2001, **20**, 5492.
25 P. B. Hitchcock, M. F. Lappert and W.-P. Leung, *J. Organomet. Chem.*, 1990, **394**, 57 and references therein.
26 (*a*) D. F. Evans, *J. Chem. Soc.*, 1959, 2003; (*b*) E. M. Schubert, *J. Chem. Educ.*, 1992, **69**, 62.
27 R. A. Anderson, D. J. Berg, L. Ferholt, K. Faegri, J. C. Green, A. Haaland, M. F. Lappert, W. P. Leung and K. Rypdal, *Acta Chem. Scand., Ser. A*, 1988, **42**, 554.
28 G. M. Sheldrick, *SHELX-97*, University of Göttingen, Germany, 1997.