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FULL PAPER

The reactivity of diazabutadienes toward low oxidation state Group 13 iodides and the synthesis of a new gallium(I) carbene analogue†

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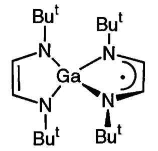
The reactions of two diazabutadiene ligands, Ar-DAB [(ArN=CH)$_2$, Ar = 2,6-Pr$^i_2$C$_6$H$_3$] and Bu^t-DAB [(Bu^{t}N=CH)$_2$] with either GaI or an AlI$_3$/Al mixture have afforded the paramagnetic compounds, [{IGa^{II}(Bu^t-DAB)}$_2$], [I$_2$Ga^{III}-(Bu^t-DAB)] and [I$_2$Al^{III}(Ar-DAB)] which have been characterised by X-ray crystallography and EPR spectroscopy. In addition, the diamagnetic, ionic complex, [I$_2$Al^{III}(Ar-DAB)]I, has been prepared and structurally characterised. The reduction of [I$_2$Ga^{III}(Ar-DAB)] with potassium metal in the presence of various Lewis bases has led to three structurally characterised compounds, [{(Et$_2$O)KGa^I(Ar-DAB)}$_2$], [{(TMEDA)KGa^I(Ar-DAB)}$_2$] and [:Ga^I(Ar-DAB)]$_2$[{K(18-crown-6)}$_2$(μ-18-crown-6)], which contain the second example of an anionic gallium(I) carbene analogue. In addition, the former two compounds display Ga ··· Ga interactions in the solid state which are unprecedented for this complex type.

Introduction

Much interest has been paid to diazabutadiene Group 13 complexes over the last 15 years and many complex types have arisen from this work. Some of the more interesting complexes that have come forward are the paramagnetic gallium(III) complex, **1**,[1] the diamagnetic gallium(II) complex, **2**,[2] and the remarkable anionic gallium(I) heterocycle, **3**,[3] which is a valence isoelectronic N-heterocyclic carbene (NHC) analogue. This anion has been obtained in an uncoordinated state (*i.e.* there is no Ga:→K coordination) as its potassium salt, [:Ga{N(Bu^t)-C$_2$H$_2$N(Bu^t)}][K(18-crown-6)(THF)$_2$],[3] and as a dimeric potassium complex, **4**.[4] Through our work with NHC-stabilised indium hydride complexes[5] we have become interested in forming indium analogues of **3** which are unknown to date. To this end we recently reported that the reaction of a sterically encumbered diazabutadiene ligand, (ArN=CH)$_2$, Ar-DAB, Ar = 2,6-Pr$^i_2$C$_6$H$_3$, with In(I)Cl yields the unusual paramagnetic indium(II) complex, **5**, *via* a 1-electron reduction of the Ar-DAB ligand by the indium centre.[6] We have now fully extended this study by (i) attempting the reduction of **5** to an indium(I) NHC analogue, (ii) investigating the reactivity of diazabutadienes toward Ga(I)I and a AlI$_3$/Al mixture and (iii) preparing a new gallium(I) NHC analogue that displays an unprecedented Ga ··· Ga interaction in the solid state. The results of these investigations are reported herein.



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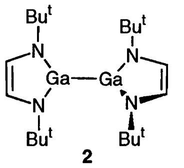

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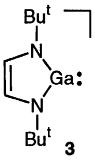

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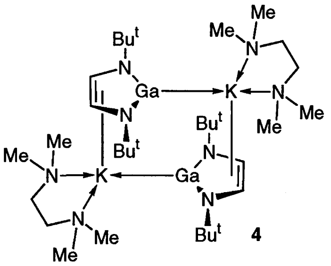

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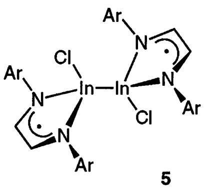

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Results and discussion

Considering the unexpected formation of **5** from the reaction of Ar-DAB with In(I)Cl it was decided to investigate the analogous reactions of diazabutadienes with Ga(I)I. This reagent is readily prepared by ultrasonicating gallium metal with 0.5 equiv. of I$_2$ in toluene.[7] When the reaction of GaI with Ar-DAB was carried out in a 2 : 1 stoichiometry in toluene at low temperature gallium metal deposition occured and a deep red solution resulted which upon work-up afforded a high yield (> 90%) of the paramagnetic gallium(III) complex, **6** (Scheme 1). Since carrying out this work Jutzi *et al.* have reported[8] a similar preparation of this compound, the spectroscopic and crystallographic data for which were found to be identical to our own and thus they will not be discussed here. It is worth noting, however, that this reaction presumably proceeds *via* a gallium(I) intermediate, [GaI(Ar-DAB)], which undergoes an intramolecular ligand reduction and subsequent disproportionation reaction to give **6** and gallium metal. The formation of **6** contrasts with the analogous reaction that gave **5**. However, the yield of **5** was low (15%) and considerable indium deposition was seen in this reaction which we believed was due to the formation of an indium analogue of **6** as the major product. In a parallel study[9] we have since confirmed this, though the paramagnetic indium(III) product formed is 5-coordinate, [InCl$_2$(THF)(Ar-DAB$^•$)], with the indium centre being additionally coordinated by a molecule of THF.

In contrast to the reactions that gave **5** and **6**, the 1 : 1 or 1 : 2 reactions of Bu^t-DAB, (Bu^{t}N=CH)$_2$, with Ga(I)I in toluene yielded predominantly the dimeric complex, **7**, but also small

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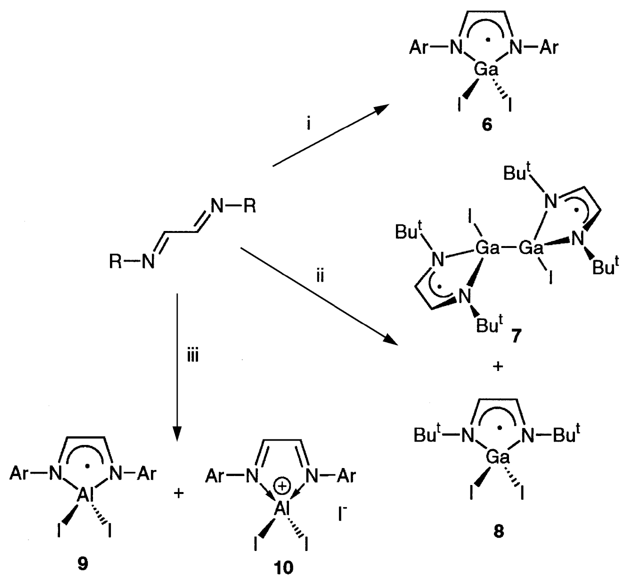
† Electronic supplementary information (ESI) available: experimental EPR spectra for compounds **9** and **7**. See http://www.rsc.org/suppdata/dt/b2/b206605j/



Scheme 1 Reagents and conditions: i, GaI, toluene, R = Ar; ii, GaI, toluene, R = Bu^t; iii, AlI_3/Al, toluene, R = Ar.

amounts of the monomeric species, **8**. It is interesting that the dimeric gallium(II) species is the major product in this reaction whereas in the analogous Ar-DAB reaction the monomeric gallium(III) compound, **6**, is in the majority. We do not know why this is but presumably it stems from the steric and electronic differences between the two diazabutadiene ligands.

An attempt was made to prepare the aluminium analogue of **6** by reacting Ar-DAB with a 1 : 2 mixture of AlI_3 and Al powder in toluene. This was successful in that over 12 hours a proportion of the aluminium powder was consumed and a deep red solution was formed. Volatiles were removed from this solution and the residue recrystallised from diethyl ether to give a good yield of the paramagnetic aluminium(III) compound, **9**. Interestingly, a trace by-product, **10**, was also isolated from the reaction mixture. This was subsequently intentionally prepared in good yield (66%) by reacting AlI_3 with one equivalent of Ar-DAB in toluene. Presumably the mechanism of formation of **9** involves the initial formation of **10** which is then reduced by the aluminium powder, followed by an intramolecular ligand reduction reaction to give **9**. It is also of interest that the reaction of Ar-DAB with AlI_3 yields an ionic product, **10**, which is comparable to the product of the 2 : 1 reaction of $GaCl_3$ with Bu^t-DAB, *viz.* $[GaCl_2(Bu^t\text{-DAB})][GaCl_4]$.[10] However, these products contrast with that from the analogous reaction of Ar-DAB with $InBr_3$ which we have recently shown to be a neutral 5-coordinate adduct, $[InBr_3(\text{Ar-DAB})]$.[11] The results of these reactions are also different to that from the reaction of BCl_3 with Ar-DAB which leads to chloroboration of the diimine and formation of [BCl(ArNC(H)(Cl)C(H)(Cl)NAr)].[12]

No meaningful NMR data could be obtained on compounds **7**–**9** due to their paramagnetic nature but all other spectroscopic data pointed towards their formulations. The ionic compound, **10**, is not paramagnetic but its ^1H NMR spectrum showed significantly broadened signals. It is thought that this is due to an exchange of I^- ligands at the aluminium centre on the NMR time scale which could proceed *via* a 5-coordinate neutral intermediate, $[AlI_3(\text{Ar-DAB})]$. This proposal seems feasible in light of the fact that the indium analogue of this compound, $[InBr_3(\text{Ar-DAB})]$, is neutral and 5-coordinate in the solid state.[11] The ^1H NMR spectrum of **10** could not be resolved when solutions of the compound were heated to 70 °C or cooled to 0 °C. Further cooling of solutions of **10** led to significant precipitation of the compound. Despite the broadening of the signals in the ^1H NMR spectrum of **10** the data suggest that the Ar-DAB ligand is acting as a localised Lewis base because the protons on the diimine backbone of the ligand resonate near those of the free ligand and the neutral indium compound, $[InBr_3(\text{Ar-DAB})]$, but significantly downfield from the imine protons in related systems incorporating reduced diazabutadiene ligands, *e.g.* **2**–**4**.

Table 1 Isotropic *g* and hyperfine coupling values for complexes **7**, **8**, **9** and **5**, obtained *via* simulation of their room temperature EPR spectra

Complex	g_{iso}	M[a]	^1H[b]	^{14}N[a]	^{127}I[c]
7	2.0030	$^{69}Ga = 0.13$ $^{71}Ga = 0.16$	0.14	0.842	0.12
8	2.0038	$^{69}Ga = 0.13$ $^{71}Ga = 0.165$	0.14	0.862	0.13
9	2.0038	$^{27}Al = 0.285$	0.59	0.67	0.04
5[6]	2.0012	$^{115}In = 2.62$ $^{113}In = 2.614$	0.50	0.50	

All isotropic hyperfine couplings in mT. [a] M refers to gallium, aluminium or indium. [b] ^1H refers to two equivalent imine protons and ^{14}N refers to the two equivalent nitrogen nuclei. [c] Two equivalent iodine nuclei simulated in **8** and **9**, but only one in **7**.

The EPR spectra of **7**–**9** were recorded at X-band frequencies. The spectrum and associated computer simulation for **8** is shown in Fig. 1.[13] This spectrum was particularly well resolved, allowing accurate spin Hamiltonian parameters to be obtained (Table 1). Similar spin Hamiltonian parameters were used to simulate the spectrum of **7** (with only one interacting ^{127}I nucleus) indicating the similarity of the radical fragment in both cases. In both gallium complexes, **7** and **8**, the spin density on the $^{69,71}Ga$ nuclei was very small (0.03%) and negligible on the ^{127}I nuclei (0.008%). Nevertheless, without this contribution from the ^{127}I nuclei an accurate simulation could not be obtained. The hyperfine couplings to the imine protons (0.14 mT) and nitrogen nuclei (*ca.* 0.85 mT) of **7** and **8** were found to be different compared to the aluminium complex, **9**, and the previously reported indium complex, **5**, where a_{iso} values close to 0.5 mT were observed (see Table 1). It is noteworthy that Jutzi *et al.* reported similar couplings of 0.41 mT and 0.7 mT for the protons and nitrogen nuclei respectively in **6**. Therefore, it seems that the presence of the *tert*-butyl groups in **7** and **8** have a significantly different influence on the spin density around the imine protons and nitrogen nuclei, compared to the

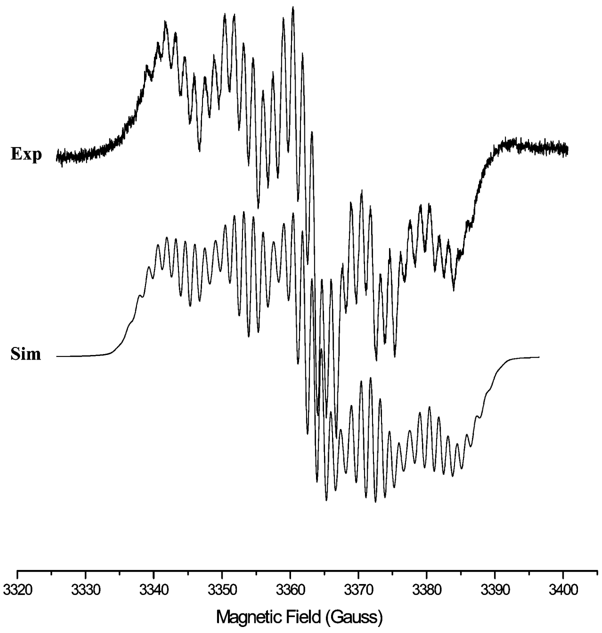


Fig. 1 X-Band EPR spectrum and computer simulation of **8** in CD_2Cl_2/C_7D_8 (50 : 50) at 298 K.

influence of the aryl groups in **5**, **6** and **9**. This influence by the *tert*-butyl groups on the electron spin density is also manifested in the hyperfine couplings to the metal centres, which was found to be 0.03% in **7** and **8**, but *ca.* 0.3% in **5** and **9**. In all complexes, **7**–**9**, the *g* values are close to free spin, indicating the essentially organic nature of the radical.

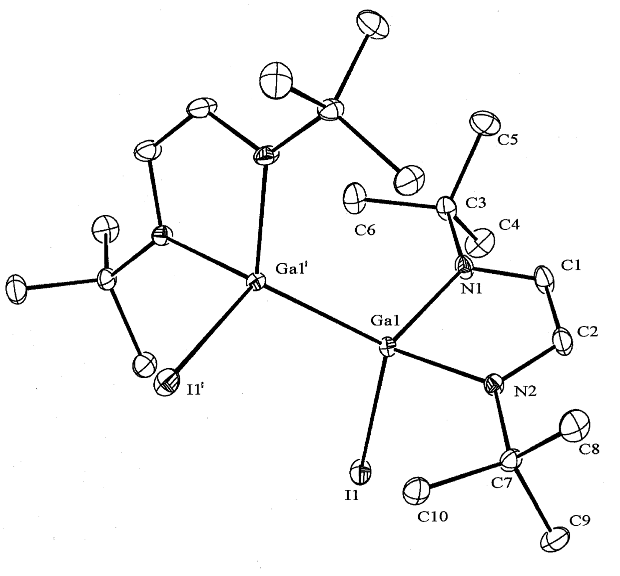


Fig. 2 Molecular structure of compound **7**. Selected bond lengths (Å) and angles (°): Ga(1)–Ga(1′) 2.4232(7), Ga(1)–I(1) 2.6169(5), Ga(1)–N(2) 1.958(3), Ga(1)–N(1) 1.966(3), N(1)–C(1) 1.322(4), N(2)–C(2) 1.333(4), C(1)–C(2) 1.395(5); N(2)–Ga(1)–N(1) 85.23(11), N(2)–Ga(1)–Ga(1′) 124.87(8), N(1)–Ga(1)–Ga(1′) 116.26(9), N(2)–Ga(1)–I(1) 103.47(8), N(1)–Ga(1)–I(1) 107.33(9), I(1)–Ga(1)–Ga(1′) 115.153(14), C(1)–N(1)–Ga(1) 108.8(2), C(2)–N(2)–Ga(1) 109.0(2), N(1)–C(1)–C(2) 118.7(3), N(2)–C(2)–C(1) 118.0(3). Symmetry operation: ′ *y*, *x*, −*z*.

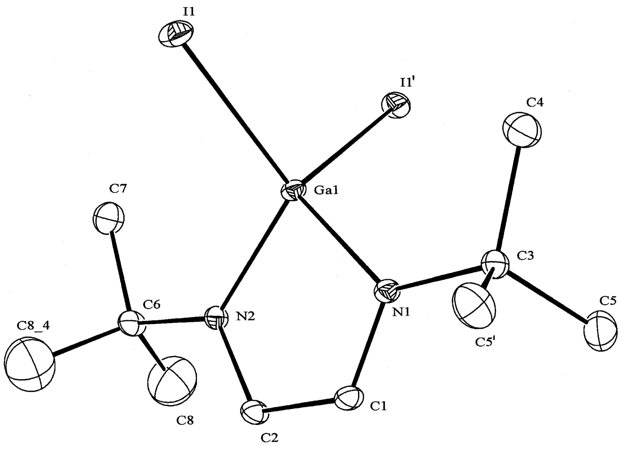


Fig. 3 Molecular structure of compound **8**. Selected bond lengths (Å) and angles (°): I(1)–Ga(1) 2.5312(7), Ga(1)–N(2) 1.896(6), Ga(1)–N(1) 1.965(6), N(1)–C(1) 1.316(10), N(2)–C(2) 1.357(10), C(1)–C(2) 1.450(11); N(1)–Ga(1)–N(2) 87.1(3), N(2)–Ga(1)–I(1) 115.89(8), N(1)–Ga(1)–I(1) 113.66(9), I(1)–Ga(1)–I(1′) 109.33(4), C(1)–N(1)–Ga(1) 108.3(5), C(2)–N(2)–Ga(1) 110.8(5), N(1)–C(1)–C(2) 118.6(7), N(2)–C(2)–C(1) 115.2(7). Symmetery operation: ′ *x*, −*y* + 3/2, *z*.

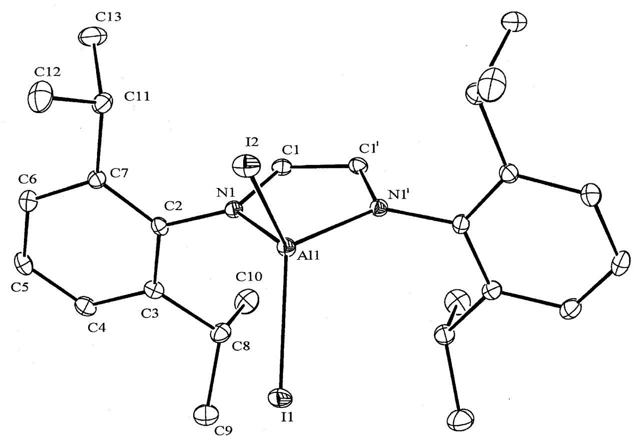


Fig. 4 Molecular structure of compound **9**. Selected bond lengths (Å) and angles (°): Al(1)–I(1) 2.4957(11), Al(1)–I(2) 2.5318(11), Al(1)–N(1) 1.889(2), N(1)–C(1) 1.337(3), C(1)–C(1′) 1.409(5); N(1)–Al(1)–N(1′) 87.42(13), N(1)–Al(1)–I(1) 116.50(7), N(1)–Al(1)–I(2) 111.93(7), I(1)–Al(1)–I(2) 110.78(4), C(1)–N(1)–Al(1) 108.93(17), N(1)–C(1)–C(1′) 116.71(14). Symmetry operation: ′ *x*, −*y* + 1/2, *z*.

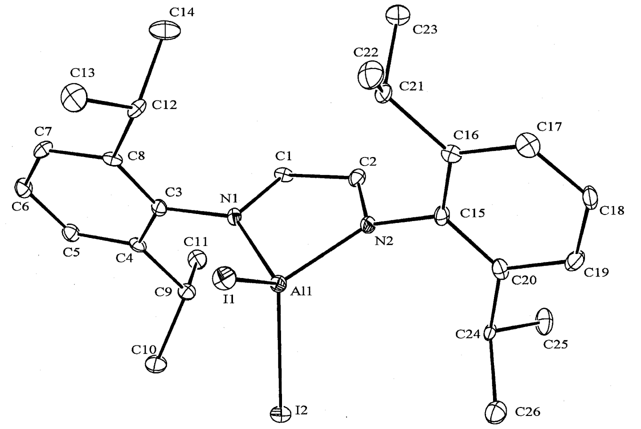


Fig. 5 Molecular structure of the cation of compound **10**. Selected bond lengths (Å) and angles (°): Al(1)–I(1) 2.491(3), Al(1)–I(2) 2.487(3), Al(1)–N(2) 1.903(8), Al(1)–N(1) 1.933(8), N(1)–C(1) 1.289(11), N(2)–C(2) 1.325(12), C(1)–C(2) 1.442(13); N(2)–Al(1)–N(1) 85.7(3), N(2)–Al(1)–I(2) 116.4(3), N(1)–Al(1)–I(2) 110.7(2), N(2)–Al(1)–I(1) 112.8(3), N(1)–Al(1)–I(1) 116.8(3), I(2)–Al(1)–I(1) 112.12(11), C(1)–N(1)–Al(1) 109.9(6), C(2)–N(2)–Al(1) 110.7(6), N(1)–C(1)–C(2) 117.7(8), N(2)–C(2)–C(1) 115.4(9).

The X-ray crystal structures of all compounds **7**–**10** were obtained and are depicted in Fig. 2–5 (see Table 2). The dimeric gallium compound, **7**, is closely related to **5** and as in that compound the bond lengths within the diazabutadiene framework show the ligand to be delocalised. The gallium centres possess distorted tetrahedral geometries and the N–Ga bond lengths and the N–Ga–N angle are close to those in **6**. Similarly, the Ga–Ga distance of 2.4232(7) Å compares well with the metal–metal interaction in related diazabutadiene complexes, *e.g.* **2** [2.333(1) Å]. Compound **8** is similar to **6** in that it is monomeric and its gallium centre has a distorted tetrahedral geometry. The Ga–N bond lengths [1.930 Å avge.] are close to those in **6** [1.9449(10)], as are the backbone C–N and C–C distances [**8**: 1.336 Å avge, 1.450(11) Å; **6**: 1.3386(15), 1.406(2) Å]. Both sets of values are comparable to those observed in the singly reduced Bu^t-DAB ligand in the related Ga(III) compound, [Ga(Bu^t-DAB)$_2$] **1**, and are strongly suggestive of delocalised diazabutadiene ligand systems.

The paramagnetic aluminium(III) compound, **9**, is isomorphous to **6** and both compounds have similar geometries and bond lengths about their metal centres, which is not surprising given the almost equivalent covalent radii for the two metals involved.[14] In addition, the bond lengths within the diazabutadiene ligand in **9** are indicative of a similar degree of delocalisation as possessed by **6**. There appears to be less delocalisation over the Ar-DAB ligand in the cation of **10** compared to **9**, despite their structural similarities. This is evidenced by the shorter N–C and longer C–C and Al–N distances in the former which is consistent with its formulation as a diamagnetic Ar-DAB adduct of the AlI$_2^+$ cation.

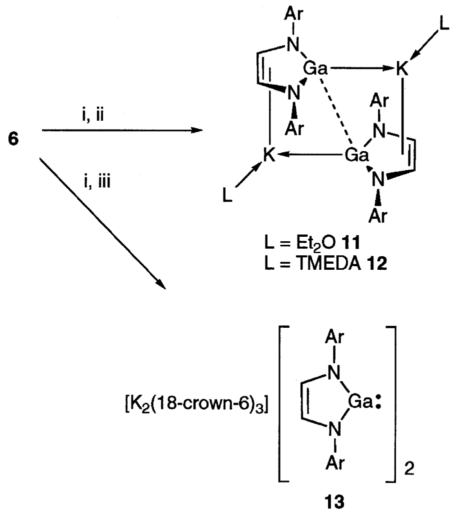
Compounds **5**, **6** and **9** seemed to be ideally suited as precursors to the Group 13 valence isoelectronic NHC analogues, [:M(Ar-DAB)]$^-$, M = In, Ga or Al, *via* reduction reactions. To

Table 2 Crystal data for compounds **7**, **8**, **9**, **10**, **11**·Et$_2$O, **12** and **13**

	7	**8**	**9**	**10**	**11**·Et$_2$O	**12**	**13**
Chemical formula	$C_{20}H_{40}Ga_2I_2N_4$	$C_{10}H_{20}GaI_2N_2$	$C_{26}H_{36}AlI_2N_2$	$C_{26}H_{36}AlI_3N_2$	$C_{64}H_{102}Ga_2K_2N_4O_3$	$C_{64}H_{104}Ga_2K_2N_8$	$C_{88}H_{144}Ga_2K_2N_4O_{18}$
M	729.80	491.80	657.35	784.25	1193.14	1203.20	1763.72
Crystal system	Tetragonal	Monoclinic	Orthorhombic	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	$P4_12_12$	$P2_1/m$	$Pnma$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a/Å	10.7330(15)	7.6790(15)	12.564(3)	10.389(2)	12.559(3)	12.615(3)	20.844(4)
b/Å	10.7330(15)	10.583(2)	21.284(4)	21.162(4)	12.623(3)	12.650(3)	26.080(5)
c/Å	24.880(5)	10.653(2)	10.412(2)	13.452(3)	12.931(3)	12.727(3)	17.719(4)
α/°	90	90	90	90	67.45(3)	82.22(3)	90
β/°	90	107.95(3)	90	95.61(3)	77.15(3)	62.52(3)	104.70(3)
γ/°	90	90	90	90	62.55(3)	66.93(3)	90
V/Å^3	2866.1(8)	823.6(3)	2784.3(10)	2943.3(10)	1677.5(6)	1655.1(6)	9317(3)
Z	4	2	4	4	1	1	4
T/K	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
μ(Mo-K$_\alpha$)/mm^{-1}	4.05	5.40	2.31	3.23	0.97	0.98	0.73
Reflections collected	34327	12390	47890	24508	26246	18217	137685
Unique reflections (R_{int})	3280 (0.0626)	1973 (0.0753)	3273 (0.0803)	5120 (0.1593)	6082 (0.0734)	5715 (0.0895)	21191(0.0964)
$R1$ ($I>2\sigma(I)$)	0.0239	0.0460	0.0280	0.0601	0.0425	0.0666	0.0690
$wR'2$ (all data)	0.0524	0.1281	0.0643	0.1355	0.1003	0.1710	0.1565

date the only known example of such an anion is **3** which is prepared in a multi-step synthesis. This involves the reaction of [Li$_2$(Bu^t-DAB)] with GaCl$_3$ to give [Ga^{III}Cl$_2${μ-Ga^{III}(Bu^t-DAB)$_2$}] which is reduced over 10 days to give the gallium(II) complex, **2**. This is further reduced with potassium metal over 10 days to give **3** or **4** depending on the presence of either 18-crown-6 or TMEDA. It is worth mentioning that two closely related neutral aluminium and gallium(I) carbene analogues, [:M[{N(Ar)CMe}$_2$CH]], M = Al[15] or Ga,[16] have been recently reported and their chemistry has begun to be explored.[17]

Unfortunately the reduction of either **5** or **9** with an excess of potassium metal in THF did not lead to the M(I) carbene analogues but instead to decomposition products which included the free Ar-DAB ligand and elemental Group 13 metal. The analogous reduction of **6** was, however, more successful. After 8 hours reaction time at room temperature and subsequent recrystallisation from diethyl ether the new gallium(I) carbene analogue, **11**, was formed in good yield (Scheme 2). In a similar fashion the reduction of the dimeric gallium(II) compound, **7**, with an excess of potassium led to a high yield of the known complex, **4**, after recrystallisation from a diethyl ether/TMEDA mixture.



Scheme 2 Reagents and conditions: i, K, THF; ii, Et$_2$O or TMEDA/Et$_2$O; iii, 18-crown-6.

The spectroscopic data for **11** are consistent with its proposed structure and are indicative of a 1 : 1 ratio of coordinated ether to gallium heterocycle. As in the case of **3** the ^{1}H and ^{13}C resonances for the olefinic fragment of the Ar-DAB backbone are significantly shifted to higher field relative to those for the free ligand, as would be expected in a reduced anionic system.

The molecular structure of **11** is depicted in Fig. 6 (Table 2). This shows the molecule to be dimeric and to sit on a centre of inversion. It can be considered as consisting of monomeric units which comprise a gallium "carbene" heterocycle η^5-coordinated to a K(Et$_2$O) fragment. Dimerisation of these fragments occurs *via* intermolecular interactions of gallium lone pairs with two potassium centres. At first glance this seems to be a very similar arrangement to that seen for **4**. The geometries of the essentially planar gallium heterocycles in **4** and **11** are similar and close to that predicted by theoretical studies for the model heterocycle, [:GaN(H)C(H)C(H)N(H)]$^-$.[18] In addition, the Ga⟶K distances in **4** [3.438(1) Å] and **11** [3.4223(10) Å], and the η^5-interactions from the heterocycles to the gallium centres are comparable [Ga–K 3.4681(5) Å **4**, 3.3784(13) Å **11**; K–N avge. 2.889 Å **4**, 2.962 Å **11**; K–C avge. 2.999 Å **4**, 2.997 Å **11**]. Despite these similarities there are also significant differences between **4** and **11**. For example, in **4** the Ga⟶K bond forms an angle of 20.8° with the C$_2$N$_2$Ga ring plane whereas in **11** this angle is only 3.4°. This in turn means

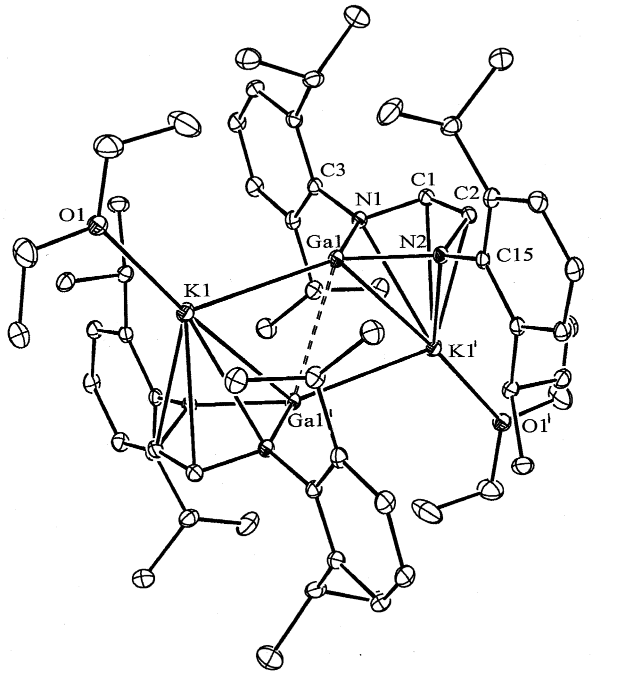


Fig. 6 Molecular structure of compound **11**. Selected bond lengths (Å) and angles (°): Ga(1)–Ga(1′) 2.8640(13), Ga(1)–N(1) 2.005(2), Ga(1)–N(2) 2.009(2), Ga(1)–K(1′) 3.3784(13), Ga(1)–K(1) 3.4223(10), K(1)–O(1) 2.718(2), K(1)–N(1′) 2.936(3), K(1)–C(1′) 2.977(3), K(1)–N(2′) 2.987(2), K(1)–C(2′) 2.997(3), K(1)–Ga(1′) 3.3784(13), C(1)–C(2) 1.356(4); N(1)–Ga(1)–N(2) 81.88(9), N(1)–Ga(1)–Ga(1′) 107.95(7), N(2)–Ga(1)–Ga(1′) 109.68(7), N(1)–Ga(1)–K(1) 138.96(6), N(2)–Ga(1)–K(1) 139.15(6), Ga(1)–N(1)–C(1) 111.05(17), C(2)–N(2)–Ga(1) 110.65(16), N(1)–C(1)–C(2) 116.8(2), N(2)–C(2)–C(1) 117.3(2). Symmetry operation: ′ $-x$, $-y$, $-z + 1$.

that the distance between the Ga centres in **4** is 4.21 Å and the heterocycle centroid–Ga–Ga angle is 106.0° whereas in **11** the same angle is 119.2° and the Ga–Ga distance is only 2.8640(13) Å. Although the difference in these Ga–Ga distances is almost 1.4 Å the shorter interaction is still longer than normally seen for Ga–Ga single bonds, *e.g.* 2.541(1) Å in [$(tmp)_2$Ga–Ga-$(tmp)_2$], tmp = 2,2,6,6-tetramethylpiperidine,[19] but not markedly so, especially considering the expected larger covalent radius of the Ga(I) centre in **11** relative to the Ga(II) centres in [$(tmp)_2$-Ga–Ga$(tmp)_2$] and other related dimers. This could mean that in **11** the two anionic gallium centres are held together, not only by an electrostatic attraction to the potassium cations but perhaps also by a partial interaction of electron density from the lone pair on each gallium centre with the p-orbital on the other. If this were the case it is only a weak interaction and it is not known why it does not occur in **4**, which should be more open to an approach of the two gallium centres, at least on steric grounds.

It was thought of sufficient worth to attempt the replacement of the coordinated Et_2O ligand of **11** with the bidentate TMEDA ligand to form the direct analogue of **4**, *i.e.* **12**, for purposes of comparison. This was readily achieved and **12** was obtained in good yield after recrystallisation from diethyl ether (Scheme 2). The spectroscopic data for **12** are very similar to those for **11** with the exception that they suggest a 1 : 1 ratio of TMEDA to each potassium centre, which would indicate chelation. The X-ray crystal structure of **12** (Fig. 7, Table 2) confirmed this and shows that the geometry of the dimeric core of the molecule is very similar to that of **11** [Ga–Ga 2.8746(15) Å; Ga(1)–K(1) 3.5318(18) Å; Ga(1)–K(1′) 3.4620(16) Å; K(1′)–C avge. 3.013 Å; K(1′)–N avge. 3.030 Å avge.]. This observation confirms that the shortness of the Ga ··· Ga interaction in **11** compared to **4** is not due to the potassium centre in the former being less electronically satisfied by the monodentate ether ligand than the bidentate TMEDA ligand in the latter.

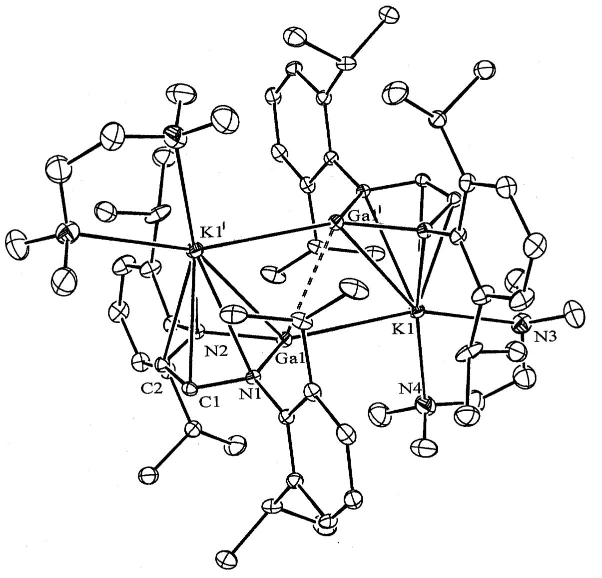


Fig. 7 Molecular structure of compound **12**. Selected bond lengths (Å) and angles (°): Ga(1)–Ga(1′) 2.8746(15), Ga(1)–N(1) 2.014(4), Ga(1)–N(2) 2.011(4), Ga(1)–K(1′) 3.4620(16), Ga(1)–K(1) 3.5318(18), K(1)–N(3) 2.996(6), K(1)–N(4) 3.055(7), K(1)–N(1′) 3.027(4), K(1)–C(1′) 3.009(5), K(1)–N(2′) 3.034(4), K(1)–C(2′) 3.016(5), K(1)–Ga(1′) 3.4620(16), C(1)–C(2) 1.350(6); N(1)–Ga(1)–N(2) 82.05(15), N(1)–Ga(1)–Ga(1′) 109.79(12), N(2)–Ga(1)–Ga(1′) 109.79(12), N(1)–Ga(1)–K(1) 138.84(10), N(2)–Ga(1)–K(1) 139.09(11), Ga(1)–N(1)–C(1) 110.4(3), C(2)–N(2)–Ga(1) 110.4(3), N(1)–C(1)–C(2) 117.2(4), N(2)–C(2)–C(1) 118.0(4). Symmetery operation: ′ $-x$, $-y + 1$, $-z$.

In order to test whether a Ga ··· Ga interaction would remain between two of the gallium heterocycles in the absence of coordinated potassium centres, compound **11** was treated with an excess of 18-crown-6 in THF and the crude product recrystallised from diethyl ether to give a good yield of **13** (Scheme 2). Again, the spectroscopic data for the gallium heterocycle are very similar to those in **11** and **12** but it could not be ascertained whether there was any heterocycle association from this data alone. As a result an X-ray crystal structure analysis of the compound was carried out and its molecular structure is shown in Fig. 8 (Table 2). The asymmetric unit contains two crystallographically independent $[:Ga(Ar\text{-}DAB)]^-$ anions and two $K(18\text{-crown-}6)_{1.5}$ cations, the latter of which are generated into dicationic units, $[(18\text{-crown-}6)K(\mu\text{-}18\text{-crown-}6)K(18\text{-crown-}6)]^{2+}$, by inversion centres. One of these is shown in Fig. 8(b) and it is clear that the terminal 18-crown-6 ligands are η^6-coordinated to a potassium centre whilst the bridging crown is η^2-coordinated to both K centres. There are no contacts between $[:Ga(Ar\text{-}DAB)]^-$ anions which strongly suggests that the Ga ··· Ga interactions in **11** and **12** are weak and will not persist in the absence of the coulombic assistance provided by the partially solvated potassium ions. The GaN_2C_2 five membered rings of both $[:Ga(Ar\text{-}DAB)]^-$ anions are positionally disordered over two sites in an 80 : 20 ratio. This disorder was successfully modelled and the geometries of the two major occupancy sets are similar so only one is shown in Fig. 8(a). Although, the $[:Ga(Ar\text{-}DAB)]^-$ units do not have an interaction with each other there appears to be a weak contact between one methyl group on each heterocycle and a potassium centre, *e.g.* C(11)–K(1) 3.432 Å. The protons on this carbon will very likely have a closer interaction but they could only be included in calculated positions so comment on such interactions is not valid. Although geometrical constraints were used to model the disorder in each $[:Ga(Ar\text{-}DAB)]^-$ anion the bond lengths and angles within the heterocycle are similar to those observed in the only other uncoordinated gallium carbene analogue, **3**, and as in that anion the Ga centres are undoubtedly 2-coordinate.

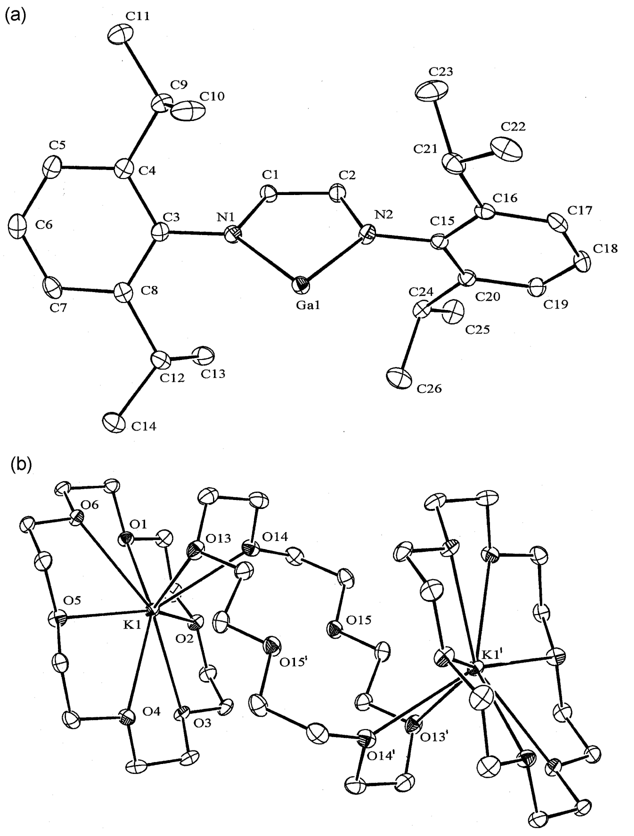


Fig. 8 Molecular structure of (a) the anion and (b) the dication of compound **13**. Selected bond lengths (Å) and angles (°): Ga(1)–N(1) 1.983(3), Ga(1)–N(2) 1.956(3), N(1)–C(1) 1.423(6), N(2)–C(2) 1.395(5), C(1)–C(2) 1.374(6), K(1)–O(1) 2.875(3), K(1)–O(2) 2.871(3), K(1)–O(3) 2.807(3), K(1)–O(4) 2.957(3), K(1)–O(5) 2.859(3), K(1)–O(6) 2.850(3), K(1)–O(13) 2.932(3), K(1)–O(14) 2.816(3), N(1)–Ga(1)-N(2) 83.02(11); Ga(1)–N(1)–C(1) 110.2(4), Ga(1)–N(2)–C(2) 114.7(3), N(1)–C(1)–C(2) 118.5(6), N(2)–C(2)–C(1) 113.6(6).

Conclusions

In conclusion we have developed a high yielding synthetic route to the monomeric, paramagnetic Group 13 diazabutadiene complexes, [I_2M^{III}(Ar-DAB)], M = Ga **6**, Al **9**, the former of which has very recently been independently reported by another group.[8] In addition, the syntheses and characterisations of the new Ga(II), Ga(III) and Al(III) complexes, [{IGa^{II}-(Bu^t-DAB)}$_2$] **7**, [I_2Ga^{III}(Bu^t-DAB)] **8** and [I_2Al^{III}(Ar-DAB)]I **10** have been described. The reduction of **6** comprises a new and facile synthetic route to Ga(I) NHC analogues, only the second example of which is reported as three potassium salts in which the alkali metal is coordinated by Et_2O **11**, TMEDA **12** or 18-crown-6 **13**. Compounds **11** and **12** exhibit Ga ··· Ga interactions which were not observed in the only other reported Ga(I) NHC analogue. We are currently developing a range of other mono- and multi-dentate Group 13 NHC analogues and investigating their coordination chemistry. The results of these investigations will be reported in forthcoming publications.

Experimental

General remarks

All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of high purity argon or dinitrogen. The solvents diethyl ether, toluene and THF were distilled over either potassium or Na/K alloy then freeze/thaw degassed prior to use. ^{1}H and ^{13}C NMR spectra were recorded on Bruker DPX400 or Jeol Eclipse 300 spectrometers in deuterated solvents and were referenced to the residual ^{1}H or ^{13}C resonances of the solvent used. Meaningful NMR spectra for **7**–**9** could not be obtained due to their paramagnetic nature. A useful ^{13}C NMR spectrum of **10** could not be obtained due to the fluxional nature of the compound in solution. The EPR spectra were recorded at room temperature on an X-band Bruker ESP 300e series spectrometer operating at 12.5 kHz field modulation in a Bruker EN801 cavity. The spectra were obtained with a 2.5 mW power. Solutions of the complexes were prepared in CD_2Cl_2/C_7D_8. The *g* values were obtained using a Bruker ER035 gaussmeter calibrated using the perylene radical cation in concentrated H_2SO_4 ($g = 2.002569$). Computer simulations were performed using the SIMFONIA Bruker software.[20] Mass spectra were recorded using a VG Fisons Platform II instrument under APCI or EI conditions. Melting points were determined in sealed glass capillaries under argon and are uncorrected. Microanalyses were obtained from the Warwick Microanalytical Service. Where reproducible micro-analyses could not be obtained the compound was either highly air sensitive, contained solvent of crystallisation or could not be separated from trace by-products. In all cases, however, all data pointed to the bulk materials having a purity of > 95%. The starting materials Ar-DAB[21] and Bu^t-DAB[22] were prepared by literature procedures and **6** was prepared by a variation of the published method.[8] All other reagents were used as received.

[{IGa(Bu^t-DAB)}$_2$] 7 and [I_2Ga(Bu^t-DAB)] 8

To a suspension of Ga metal (0.24 g, 3.4 mmol) in toluene (15 ml) was added I_2 (0.43 g, 1.7 mmol) at 25 °C. The mixture was sonicated until the solution had become colourless and a pale green precipitate was produced. To this suspension was added a solution of Bu^t-DAB (0.57 g, 3.4 mmol) in toluene (15 ml) and the resulting suspension stirred for 4 hours to yield a red solution. This was filtered, concentrated to *ca.* 10ml and placed at −30 °C overnight to yield a mixture of **7** as dark green crystals (0.37 g, 32%) and **8** as red crystals (0.06 g, 4% based on Bu^t-DAB) which were manually separated.

Data for **7**: mp 126–131 °C; MS APCI: *m*/*z* (%) 492 (Ar-DABGaI_2^+, 27), 169 (Ar-DABH$^+$, 100); IR (Nujol) ν/cm^{-1} 1634 (m), 1527(s), 1260(s), 1204(m), 779(m); $C_{20}H_{40}Ga_2I_2N_4$ requires C 32.97, H 5.52, N 7.68%; found: C 33.43, H 5.64, N 7.74%.

Data for **8**: mp 85–92 °C; MS APCI: *m*/*z* (%) 492 (M$^+$, 5), 169 (Ar-DABH$^+$, 100); IR (Nujol) ν/cm^{-1} 1634(m), 1265(s), 1199(m), 1015(m), 799(m); $C_{10}H_{20}N_2GaI_2$ requires C 24.42, H 4.10, N 5.70%; found: C 24.66, H 4.14, N 5.48%.

[I_2Al(Ar-DAB)] 9

To a suspension of Al powder (0.073 g, 2.7 mmol) in toluene (15 ml) was added I_2 (0.342 g, 0.135 mmol) at 25 °C. The resulting suspension was sonicated for 4 hours to yield an AlI_3/Al mixture. A solution of Ar-DAB (1.0 g, 2.7 mmol) in toluene (15 ml) was added to this over 5 min at 25 °C to give an immediate deep red colour to the suspension. This was stirred overnight during which time a proportion of the Al powder was seen to dissolve. Volatiles were removed *in vacuo* and the residue extracted into Et_2O (20 ml). Cooling to −30 °C yielded red crystals of **9** overnight (0.70 g, 40% based upon Ar-DAB), mp 224–227 °C; MS APCI: *m*/*z* (%) 377 (Ar-DABH$^+$, 100), 531 (M$^+$ − I, 61); IR (Nujol) ν/cm^{-1} 1516(s), 1219(s), 1055(s), 886(m), 789(m); $C_{26}H_{36}N_2AlI_2$ requires C 47.50, H 5.52, N 4.26%; found: C 47.16, H 5.57, N 4.10%.

[I_2Al(Ar-DAB)]I 10

To a solution of AlI_3 (0.54 g, 1.33 mmol) in toluene (15 ml) was added a solution of Ar-DAB (0.50 g, 1.33 mmol) in toluene (15 ml) over 5 min at 25 °C. The solution immediately became a deep red colour and was stirred for 5 hours whereupon volatiles were removed *in vacuo* and the residue extracted into Et_2O (20 ml) and the resulting solution placed at −30 °C to yield red crystals of **10** overnight (0.69 g, 66%), mp 163–176 °C (decomp.); ^{1}H NMR (400 MHz, C_6D_6, 300 K) δ 0.95 (br, 24H,

CH_3), 2.98 (br, 4H, CH), 7.02 (br, 6H, ArH), 8.05 (br, 2H, NCH); MS EI: *m*/*z* (%) 332 (Ar-DAB − Pr^{i+}, 100), 531 (M^+ − 2I, 10); IR (Nujol) *ν*/cm^{-1} 1532(s), 1276(s), 1255(m), 1107(s), 799(m).

[{(Et_2O)KGa(Ar-DAB)}$_2$] 11

A solution of **6** (0.75 g, 1.07 mmol) in THF (15 ml) was stirred over a potassium mirror (0.80 g, 20 mmol) at 25 °C for 8 hours after which the yellow-orange solution was filtered and volatiles removed *in vacuo*. The residue was extracted into Et_2O (20 ml) and the resulting solution was concentrated to *ca.* 10 ml and cooled to −30 °C overnight to yield **11** as red crystals (0.45 g, 75%), mp 180–187 °C (decomp.); ^{1}H NMR (400 MHz, C_6D_6, 300 K) *δ* 1.28 (t, 12H, $^3J_{HH}$ = 6.4 Hz, CH_3), 1.46 (d, 48H, $^3J_{HH}$ = 6.8 Hz, CH_3), 3.44 (q, 8H, $^3J_{HH}$ = 6.4 Hz, CH_2), 3.83 (sept., 8H, $^3J_{HH}$ = 6.8 Hz, CH), 6.48 (s, 4H, NCH), 7.23 (t, 4H, $^3J_{HH}$ = 7.4 Hz, *p*-Ar), 7.37 (d, 8H, $^3J_{HH}$ = 7.4 Hz, *m*-Ar); ^{13}C NMR (100.6 MHz, C_6D_6, 300 K) *δ* 15.3 (CH_2*C*H_3), 25.3 (CH*C*H_3), 28.0 (CH), 65.6 (CH_2), 122.5 (CN), 122.8 (*m*-ArC), 123.7 (*p*-ArC), 145.8 (*o*-ArC), 150.2 (*ipso*-ArC); MS EI: *m*/*z* (%) 377 [DAB^+, 5], 189 [$ArNCH^+$, 100]; IR (Nujol) *ν*/cm^{-1} 1583(s), 1557(m), 1255(s), 1096(s), 927(m).

[{(TMEDA)KGa(Ar-DAB)}$_2$] 12

To a solution of **11** (0.40 g, 0.76 mmol) in Et_2O (25 ml) at −78 °C was added TMEDA (0.40 g, 3.5 mmol) and the resulting solution warmed to room temperature and stirred for 4 hours after which time volatiles were removed *in vacuo* and the residue extracted into Et_2O (10 ml). The resulting solution was cooled to −30 °C overnight to yield **12** as red crystals (0.31 g, 68%), mp 163–166 °C (decomp.); ^{1}H NMR (400 MHz, C_6D_6, 300 K) *δ* 1.41 (d, 24H, $^3J_{HH}$ = 6.9 Hz, CH_3), 1.43 (d, 24H, $^3J_{HH}$ = 6.9 Hz, CH_3), 2.05 (2, 24H, NCH_3), 2.20 (s, 8H, NCH_2), 3.82 (sept., 8H, $^3J_{HH}$ = 6.9 Hz, CH), 6.42 (s, 4H, NCH), 7.23 (t, 4H, $^3J_{HH}$ = 7.5 Hz, *p*-Ar), 7.32 (d, 8H, $^3J_{HH}$ = 7.5 Hz, *m*-Ar); ^{13}C NMR (100.6 MHz, C_6D_6, 300 K) *δ* 26.0 (CH*C*H_3), 28.7 (CH), 46.2 (NCH_3), 58.2 (NCH_2), 123.1 (CN), 123.4 (*m*-ArC), 124.3 (*p*-ArC), 146.3 (*o*-ArC), 151.0 (*ipso*-ArC); MS EI: *m*/*z* (%) 115 [$TMEDAH^+$, 100], 189 [$ArCNH^+$, 3]; IR (Nujol) *ν*/cm^{-1} 1588(s), 1562(m), 1245(s), 1096(s) 1081(m).

[:Ga(Ar-DAB)]$_2$[{K(18-crown-6)}$_2$(μ-18-crown-6)] 13

To a solution of **11** (0.29 g, 0.26 mmol) in THF (15 ml) at −50 °C was added a solution of 18-crown-6 (0.30 g, 1.14 mmol) in THF (15 ml). The resulting orange solution was allowed to warm to 25 °C and was stirred for 2 hours whereupon volatiles were removed *in vacuo*. The residue was extracted into Et_2O (10 ml) and the resulting solution cooled to −30 °C to yield **13** as orange needles (0.27 g, 59%), mp 134–139 °C; ^{1}H NMR (400 MHz, C_6D_6, 300 K) *δ* 1.58 (d, 24H, $^3J_{HH}$ = 6.9 Hz, CH_3), 1.64 (d, 24H, $^3J_{HH}$ = 6.9 Hz, CH_3), 3.27 (s, 72H, OCH_2), 4.45 (sept., 8H, $^3J_{HH}$ = 6.9 Hz, CH), 6.82 (s, 4H, NCH), 7.28 (t, 4H, $^3J_{HH}$ = 7.5 Hz, *p*-Ar), 7.43 (d, 8H, $^3J_{HH}$ = 7.5 Hz, *m*-Ar); ^{13}C NMR (100.6 MHz, C_6D_6, 300 K) *δ* 26.0 (CH_3), 26.7 (CH_3), 28.6 (CH), 70.7 (CH_2), 122.2 (CN), 122.4 (*m*-ArC), 122.7 (*p*-ArC), 146.5 (*o*-ArC), 152.6 (*ipso*-ArC); MS EI: *m*/*z* (%) 443 [Ga(Ar-DAB)$^+$ 17], 377 [DAB^+, 31], 265 [18-crown-6$^+$, 100]; IR (Nujol) *ν*/cm^{-1} 1573(s), 1552 (m), 1255 (s), 1112(s) 794(s); $C_{88}H_{144}O_{18}N_4Ga_2K_2$ requires C 59.93, H 8.23, N 3.18%; found: C 58.92, H 8.25, N 3.10%.

Structure determinations

Crystals of **7**–**13** suitable for X-ray structure 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)[23] using all unique data. Crystal data, details of data collections and refinements are given in Table 1. The molecular structures of the complexes are depicted in Fig. 2–8 and show ellipsoids at the 30% probability level.

CCDC reference numbers 189504–189510.

See http://www.rsc.org/suppdata/dt/b2/b206605j/ for crystallographic data in CIF or other electronic format.

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References and notes

1 (*a*) F. G. N. Cloke, G. R. Hanson, M. J. Henderson, P. B. Hitchcock and C. L. Raston, *J. Chem. Soc., Chem. Commun.*, 1989, 1002; (*b*) T. Pott, P. Jutzi, B. Neumann and H. G. Stammler, *Organometallics*, 2001, **20**, 1965.
2 D. S. Brown, A. Decken and A. H. Cowley, *J. Am. Chem. Soc.*, 1995, **117**, 5421.
3 E. S. Schmidt, A. Jockisch and H. Schmidbaur, *J. Am. Chem. Soc.*, 1999, **121**, 9578.
4 E. S. Schmidt, A. Schier and H. Schmidbaur, *J. Chem. Soc., Dalton Trans.*, 2001, 505.
5 C. Jones, *Chem. Commun.*, 2001, 2293.
6 R. J. Baker, R. D. Farley, C. Jones, M. Kloth and D. M. Murphy, *Chem. Commun.*, 2002, 1196.
7 M. L. H. Green, P. Mountford, G. J. Smout and S. R. Peel, *Polyhedron*, 1990, **9**, 2763.
8 T. Pott, P. Jutzi, W. Kaim, W. W. Schoeller, B. Neumann, A. Stammler, H. G. Stammler and M. Wanner, *Organometallics*, 2002, **21**, 3169.
9 R. J. Baker, C. Jones and M. Kloth, unpublished results.
10 J. A. C. Clyburne, R. D. Culp, S. Kamepalli, A. H. Cowley and A. Decken, *Inorg. Chem.*, 1996, **35**, 6651.
11 R. J. Baker, A. J. Davies, C. Jones and M. Kloth, *J. Organomet. Chem.*, 2002, **656**, 203.
12 F. S. Mair, R. Manning, R. G. Pritchard and J. E. Warren, *Chem. Commun.*, 2001, 1136.
13 The experimental EPR spectra of **7** and **9** are included as ESI †.
14 J. Emsley, *The Elements*, Clarendon Press, Oxford, 2nd edn., 1991.
15 C. Cui, H. W. Roesky, H. G. Schmidt, M. Noltemeyer, H. Hao and F. Cimpoesu, *Angew. Chem., Int. Ed.*, 2000, **39**, 4274.
16 N. J. Hardman, B. E. Eichler and P. P. Power, *Chem. Commun.*, 2000, 1991.
17 See for example: N. J. Hardman, P. P. Power, J. D. Gorden, C. L. B. Macdonald and A. H. Cowley, *Chem. Commun.*, 2001, 1866.
18 A. Sundermann, M. Reiher and W. W. Scoeller, *Eur. J. Inorg. Chem.*, 1998, 305.
19 G. Linti, R. Frey and M. Schmidt, *Z. Naturforsch., Teil B*, 1994, **49**, 958.
20 WINEPR SIMFONIA Version 1.25, Bruker Analytische Messtechnick GmbH, 1996.
21 L. Jafarpour, E. D. Stevens and S. P. Nolan, *J. Organomet. Chem.*, 2000, **606**, 49.
22 J. M. Kleigman and R. K. Barnes, *Tetrahedron*, 1970, **26**, 2555.
23 G. M. Sheldrick, SHELXL-97, University of Göttingen, 1997.