



Synthesis and further reactivity studies of some transition metal gallyl complexes

Cameron Jones*, David P. Mills, Richard P. Rose, Andreas Stasch, William D. Woodul

School of Chemistry, Monash University, P.O. Box 23, Clayton, VIC 3800, Australia

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ABSTRACT

Reactions of the anionic gallium(I) heterocycle salt, $[\text{K}(\text{tmeda})][\text{Ga}(\text{DAB})]$ ($\text{DAB} = \{\text{N}(\text{Dip})\text{C}(\text{H})_2\}_2$; $\text{Dip} = \text{C}_6\text{H}_3\text{Pr}^i\text{-2,6}$), with a series of groups 6–9 and 11 metal halide complexes have given rise to the metal gallyl complexes, $[\text{CpCr}(\text{IMes})\{\text{Ga}(\text{DAB})\}]$ ($\text{IMes} = :C\{\text{Mes}\}\text{NC}(\text{H})_2$; $\text{Mes} = \text{mesityl}$), $[\text{M}(\text{tmeda})\{\text{Ga}(\text{DAB})\}_2]$ ($\text{M} = \text{Mn, Fe or Co}$) and $[\text{Cu}(\text{dppe})\{\text{Ga}(\text{DAB})\}]$ ($\text{dppe} = 1,2\text{-bis}(\text{diphenylphosphino})\text{ethane}$). The majority of the complexes have been crystallographically characterized. The reactivity of the previously reported copper(I) gallyl complex, $[(\text{IPr})\text{Cu}\{\text{Ga}(\text{DAB})\}]$ ($\text{IPr} = :C\{\text{Dip}\}\text{NC}(\text{H})_2$), towards a variety of unsaturated substrates has been explored. Three crystallographically characterized complexes have arisen from this phase of the study, viz. $[(\text{IPr})\text{CuC}\equiv\text{CPh}]$, $[(\text{IPr})\text{Cu}\{\text{Ga}(\text{DAB})\}(\text{C}\equiv\text{NBU}^t)]$ and $[(\text{IPr})\text{Cu}\{\kappa^1\text{-OC}(\text{O})\text{C}(\text{C}=\text{NHDip})(\text{NHDip})\}]$. The results of these investigations show that the reactivity of $[(\text{IPr})\text{Cu}\{\text{Ga}(\text{DAB})\}]$ is significantly different to that of related copper boryl complexes.

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1. Introduction

Since Cotton's preparation of the quadruply bonded dianion, $[\text{Re}_2\text{Cl}_8]^{2-}$ [1], the chemistry of metal–metal bonded compounds has rapidly expanded [2]. Interest in this field has been invigorated over the last decade with reports on a variety of unprecedented compound types. These include chromium(I) dimers bearing quintuple Cr–Cr bonding interactions, e.g. $[\text{Ar}'\text{CrCrAr}']$ ($\text{Ar}' = \text{bulky terphenyl}$) [3], singly bonded zinc(I) dimers, e.g. $\text{Cp}^*\text{ZnZnCp}^*$ ($\text{Cp}^* = \text{C}_5\text{Me}_5$) [4], and related Mg–Mg bonded magnesium(I) dimers, e.g. LMgMgL ($\text{L} = \text{bulky guanidinate or } \beta\text{-diketiminato}$) [5]. In addition, compounds containing unsupported heteronuclear M–M' bonds ($\text{M} = \text{p-block metal, M}' = \text{d-block metal}$) have been widely studied in recent years. We have made a contribution to this area through a systematic study of the coordination chemistry of the anionic gallium(I) heterocycle, $[\text{Ga}(\text{DAB})]^-$ **1** ($\text{DAB} = \{\text{N}(\text{Dip})\text{C}(\text{H})_2\}_2$; $\text{Dip} = \text{C}_6\text{H}_3\text{Pr}^i\text{-2,6}$), which is a valence isoelectronic analogue of the important N-heterocyclic carbene (NHC) class of ligand [6]. Like NHCs this anion has proved very nucleophilic, a property which has led to its use as a gallium donor ligand in the formation of complexes with more than 45 elements from all blocks of the periodic table [7,8]. It is of note that during the course of this study, the coordination chemistry of **1** has been found to be comparable with that of gallium diyls ($:\text{Ga}^i\text{R}$) [9] and neutral gallium(I) heterocycles (e.g. six-membered $[\text{Ga}(\text{Nacnac})]$

($\text{Nacnac} = \{\text{N}(\text{Dip})\text{C}(\text{Me})_2\text{CH}\}$) [10] and four-membered $[\text{Ga}(\text{Giso})]$ ($\text{Giso} = \{\text{N}(\text{Dip})\}_2\text{CNCy}_2$, $\text{Cy} = \text{cyclohexyl}$) [11,12]).

The coordination chemistry of **1** towards transition metal fragments has been particularly fruitful. This work has highlighted the fact that, like most NHCs, the gallium(I) heterocycle is a strong σ -donor ligand (having a largely sp-hybridized Ga lone pair), but a weak π -acceptor [8(1)]. This is despite it having an effectively empty Ga p-orbital orthogonal to the heterocycle plane. Moreover, its transition metal complexes have been compared to those of cyclic boryl ligands, e.g. $-\text{B}(\text{cat})$ and $-\text{B}(\text{pin})$ ($\text{cat} = \text{catecholato}$, $\text{pin} = \text{pinacolato}$), which are finding wide use as catalysts for a number of synthetic transformations [8(d,g)]. In this respect, it is noteworthy that the direct boron analogue of **1**, viz. $[\text{B}(\text{DAB})]^-$, has recently been reported [13], and its transition metal complexes are emerging as reagents for the borylation of unsaturated substrates [14]. We are interested in examining the applicability of d-block complexes of **1** for related gallylations. Here, we report the synthesis and structural characterization of some first row d-block metal gallyl complexes. In addition, we describe the unexpected outcomes of the reactions of these, and other metal gallyls, with a variety of unsaturated substrates.

2. Results and discussion

2.1. Preparation and characterization of metal gallyl complexes

Our previous work has shown that the preparation of transition metal gallyl complexes can be achieved *via* salt elimination

* Corresponding author. Tel.: +61 (0) 3 9902 0391; fax: +61 (0) 3 9905 4597.
E-mail addresses: cameron.jones@monash.edu, cameron.jones@sci.monash.edu.au (C. Jones).

reactions between $[K(\text{tmeda})][\mathbf{1}]$ and metal halide precursors $[\mathbf{8}]$. However, for these to be successful, the metal halide precursors need to incorporate electron rich ligands, e.g. N-heterocyclic carbenes (NHCs), bidentate phosphines, amines etc. In the absence of such ligands the gallyl anion tends to reduce the metal halide precursor, yielding product mixtures.

As no group 6 metal gallyl complexes have been prepared using salts of $\mathbf{1}$, we sought to achieve this utilizing a suitable chromium halide precursor. To this end, the 1:1 reaction of the chromium(II) NHC complex, $[\text{CpCr}(\text{IMes})\text{Cl}]$ ($\text{IMes} = \text{:C}(\text{Mes})\text{NC}(\text{H})_2$; Mes = mesityl) with $[K(\text{tmeda})][\mathbf{1}]$ gave an excellent yield of the 14-electron chromium gallyl, $\mathbf{2}$ (Scheme 1). In contrast, the 2:1 reaction of $[K(\text{tmeda})][\mathbf{1}]$ with the related chromium(III) complex, $[\text{CpCr}(\text{IMes})\text{Cl}_2]$, yielded the paramagnetic gallium(II) dimer, $[\{\text{ClGa}(\text{DAB}\cdot)\}_2]$ $[\mathbf{8}(\text{o})]$ and unidentified reduced chromium containing products.

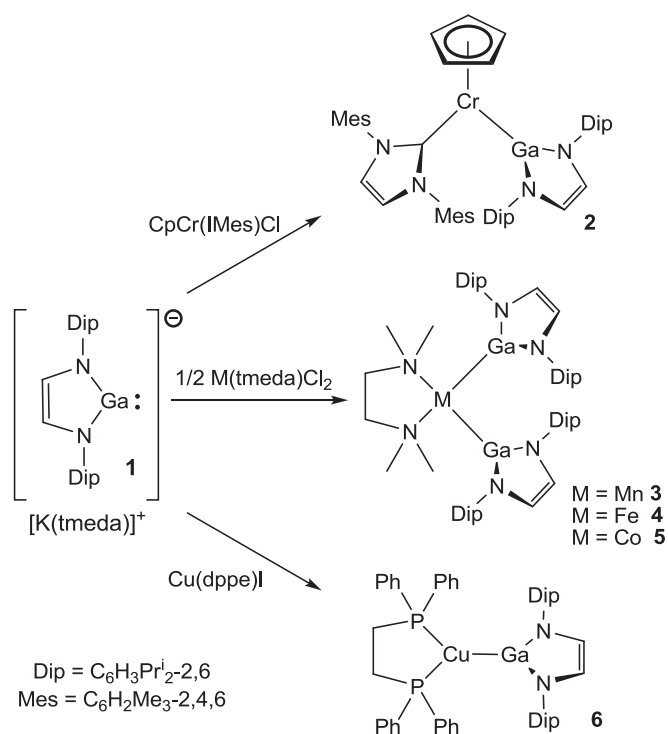
Due to the paramagnetic nature of $\mathbf{2}$ no meaningful NMR spectroscopic data could be obtained for it. The magnetic susceptibility of the compound in solution at 298 K ($\mu_{\text{eff}} = 2.45 \mu_{\text{B}}$ Evans method) suggests it is a low-spin d^4 complex. It is of note that, while most reported $\text{CpCr}(\text{II})$ complexes are low spin $[\mathbf{15}]$, the chromium halide precursor complex, $[\text{CpCr}(\text{IMes})\text{Cl}]$, is high spin with four unpaired electrons ($\mu_{\text{eff}} = 4.62 \mu_{\text{B}}$) $[\mathbf{16}]$. The apparent difference in spin multiplicity between this compound and $\mathbf{2}$ can be explained by the demonstrated stronger σ -donor ability of $\mathbf{1}$ $[\mathbf{8}(\text{d,g})]$, compared to the chloride anion. No EPR measurement of $\mathbf{2}$ was attempted as it was assumed that the compound is likely to be EPR silent, as are $[\text{CpCr}(\text{IMes})\text{Cl}]$ and other paramagnetic chromium(II) complexes $[\mathbf{16}]$.

The X-ray crystal structure of $\mathbf{2}$ was determined and its molecular structure (Fig. 1) shows it to be a two legged “piano-stool” complex with a rather obtuse $\text{C}_{(\text{carbene})}\text{—Cr—Ga}$ angle of $110.52(6)^\circ$ (cf. 97.98° in $[\text{CpCr}(\text{IMes})\text{Ph}]$ $[\mathbf{16}]$). The Ga—Cr bond length of the complex ($2.5800(5) \text{ \AA}$) is long and in fact is outside the known range for such interactions ($2.390\text{—}2.490 \text{ \AA}$) $[\mathbf{17}]$. Compound $\mathbf{2}$ is perhaps best compared with the closely related species, $[(\text{C}_5\text{H}_4\text{Me})_2\text{Cr}\{\text{Ga}(\text{DAB})\}]$

$[\mathbf{8}(\text{l})]$, which was prepared via the reaction of the chromocene, $[\text{Cr}(\text{C}_5\text{H}_4\text{Me})_2]$, with the digallane(4), $[\{\text{Ga}(\text{DAB})\}_2]$. The significantly shorter Cr—Ga distance in that compound ($2.4231(11) \text{ \AA}$) can be attributed to the expected smaller chromium(III) ionic radius relative to the chromium(II) ion in $\mathbf{2}$. Moreover, the steric crowding at the Cr center of $\mathbf{2}$ is considerably greater than in the chromium(III) complex.

We have previously prepared the first row d-block metal bis(gallyl) complexes, $[\text{M}(\text{tmeda})\{\text{Ga}(\text{DAB})\}_2]$ ($\text{M} = \text{Ni}$ $[\mathbf{8}(\text{d})]$ or Zn $[\mathbf{8}(\text{e})]$) via the 2:1 reactions of $[K(\text{tmeda})][\text{Ga}(\text{DAB})]$ with $[\text{MCl}_2(\text{tmeda})]$. In order to extend this compound series to the lighter transition metals, related reactions were carried out with $[\text{MCl}_2(\text{tmeda})_n]$ ($\text{M} = \text{Mn}$, Fe or Co ; $n = 1$ or 2). These afforded the corresponding bis(gallyl) complexes, $\mathbf{3}\text{—}5$, in low isolated yields (Scheme 1). Of note is the fact that the reaction that gave $\mathbf{3}$, also afforded a very low yield ($<2\%$) of the tmeda bridged dimeric gallium(III) heterocyclic complex, $[\{\text{DAB}\text{Ga}(\text{Cl})(\mu\text{-Me}_2\text{NCH}_2\text{-})\}_2]$, presumably via a redox side reaction. No data for this compound was obtained, but details of its crystal structure can be found in the Supplementary Material. In addition, a few crystals of the paramagnetic oxo-bridged gallium(III) complex, $[\{\text{DAB}\text{Ga}(\text{OH})(\mu\text{-O})\}_2]$, were isolated from the reaction that gave $\mathbf{5}$. This compound probably formed due to the presence of adventitious oxygen and/or water in the reaction mixture, though the exact mechanism of its formation is not known. It was crystallographically characterized and subsequently rationally synthesized via the treatment of the digallane(4), $[\{\text{Ga}(\text{DAB})\}_2]$, with N_2O (see Supplementary Material for details).

All complexes $\mathbf{3}\text{—}5$ are paramagnetic and, as a result, meaningful NMR spectroscopic data could not be obtained for them. Their room temperature solution state magnetic moments were determined to be $\mathbf{3}$ $\mu_{\text{eff}} = 5.71 \mu_{\text{B}}$, $\mathbf{4}$ $\mu_{\text{eff}} = 5.12 \mu_{\text{B}}$ and $\mathbf{5}$ $\mu_{\text{eff}} = 2.21 \mu_{\text{B}}$ (Evans method). These values are consistent with the Mn and Fe complexes being high-spin d^5 and d^6 systems respectively, while the value for the Co complex approximates to that expected for a low-spin d^7 complex.



Scheme 1.

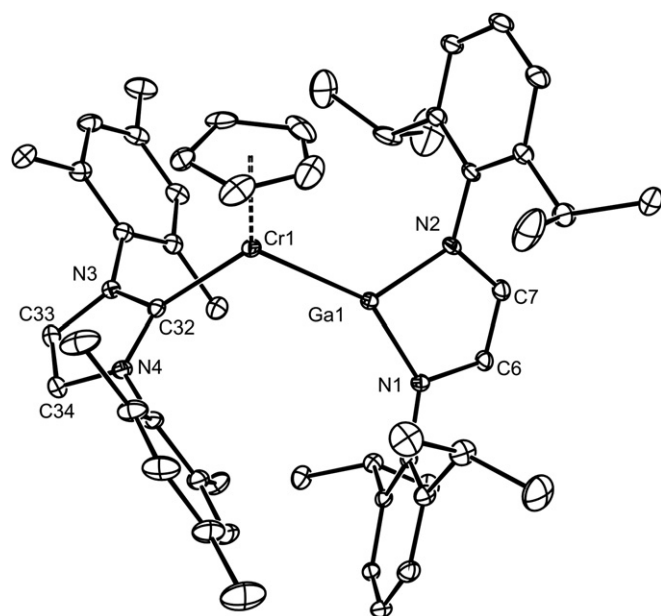


Fig. 1. Molecular structure of $\mathbf{2}$ (25% probability ellipsoids; hydrogen atoms omitted). Selected bond lengths (\AA) and angles ($^\circ$): Ga(1)—N(1) 1.9209(19), Ga(1)—N(2) 1.923(2), Ga(1)—Cr(1) 2.5800(5), Cr(1)—C(32) 2.115(2), Cr—Cp cent. 1.985(2), N(3)—C(32) 1.373(3), N(4)—C(32) 1.356(3), N(1)—Ga(1)—N(2) $84.67(8)$, N(4)—C(32)—N(3) $103.4(2)$, C(32)—Cr(1)—Ga(1) $110.52(6)$, Cp cent.—Cr(1)—Ga(1) $123.42(5)$, Cp cent.—Cr(1)—C(32) 125.88 .

In order to assess the coordination geometries of the complexes in the solid state, they were crystallographically characterized. The molecular structures of **4** and **5** are depicted in Figs. 2 and 3 and reveal their metal centers to have distorted tetrahedral and square planar environments respectively. Although the quality of the X-ray crystal diffraction data for **3** was poor, a partial refinement of its structure showed it to have a tetrahedral coordination geometry similar to that of **4**. That these complexes are high spin in solution is to be expected given their solid state geometries. Furthermore, it is not uncommon for square planar Co(II) complexes to have low-spin electronic configurations [18]. For comparison, the Ni and Zn analogues of these compounds, viz. $[M(\text{tmeda})\{\text{Ga}(\text{DAB})\}_2]$ ($M = \text{Ni}$ or Zn), are square planar [8(d)] and tetrahedral [8(e)] respectively, and both are diamagnetic.

The Fe–Ga distances in **4** are at the high end of the known range for such interactions (2.25–2.55 Å) [17], and are significantly longer than in the only other iron complex of **1**, viz. $[\text{K}(\text{tmeda})][\text{Fe}(\text{CO})_4\{\text{Ga}(\text{DAB})\}]$ (2.3068(8) Å) [8(r)]. In contrast, the Co–Ga distances in **5** are at the low end of the reported range (2.23–2.76 Å) [17], but longer than in related cobalt gallyl complexes, e.g. $[\text{K}(\text{tmeda})][\text{CpCo}(\text{CO})\{\text{Ga}(\text{DAB})\}]$ (2.2347(7) Å) [8(l)]. It is worthy of note that there is a short non-bonded Ga···Ga interaction (2.970(2) Å) in the structure of **5**, as was the case in the isomorphous compound, $[\text{Ni}(\text{tmeda})\{\text{Ga}(\text{DAB})\}_2]$ (2.910(2) Å) [8(d)]. Both interactions are comparable to close B···B separations that have been observed in related cobalt(II) and platinum(II) bis(boryl) complexes, e.g. *cis*- $[\text{Co}\{\text{B}(\text{cat})\}_2(\text{PMe}_3)_3]$ and *cis*- $[\text{Pt}\{\text{B}(\text{cat})\}_2(\text{PPh}_3)_2]$ [19], the origins of which are not fully clear.

Attempts to prepare the copper(II) analogue of **3–5** by treatment of $[\text{CuCl}_2(\text{tmeda})]$ with 2 equivalents of $[\text{K}(\text{tmeda})][\text{Ga}(\text{DAB})]$ were not successful and instead resulted in the deposition of copper metal. This outcome attests to the reducing ability of **1**. In order to access a copper gallyl complex, the copper(I) halide precursor, $[\{\text{Cu}(\text{dppe})\}_2]$ (*dppe* = 1,2-bis(diphenylphosphino)ethane), was chosen to react with $[\text{K}(\text{tmeda})][\text{Ga}(\text{DAB})]$. The reasoning here was that a copper(I) gallyl complex should be more stable to internal redox processes than a copper(II) bis(gallyl) species. In addition, the bulky *dppe* ligand should afford more kinetic protection to the formed complex than would *tmeda*. This strategy was successful as the reaction of half an equivalent of $[\{\text{Cu}(\text{dppe})\}_2]$ with $[\text{K}(\text{tmeda})][\text{Ga}(\text{DAB})]$ afforded the red monomeric copper(I) gallyl, **6**, in moderate yield (Scheme 1).

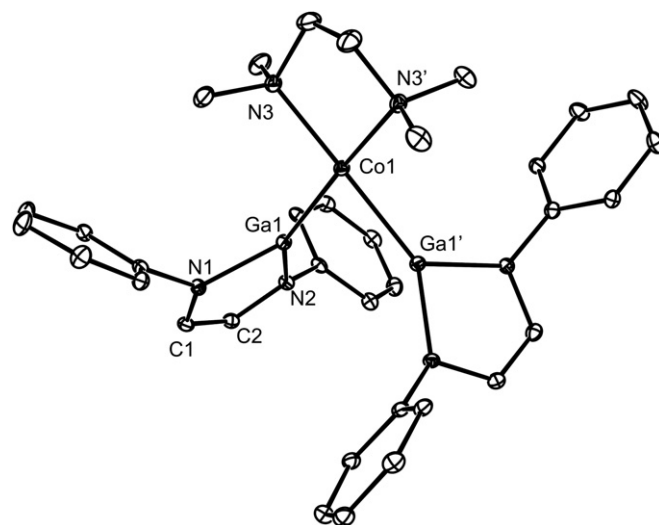


Fig. 3. Molecular structure of **5** (25% probability ellipsoids; hydrogen atoms and isopropyl groups omitted). Selected bond lengths (Å) and angles (°): Ga(1)–N(2) 1.898(2), Ga(1)–N(1) 1.915(2), Ga(1)–Co(1) 2.3331(6), Co(1)–N(3) 2.085(2), Ga(1')–Co(1)–Ga(1) 79.06(3), N(3)–Co(1)–N(3') 84.84(13), N(2)–Ga(1)–N(1) 86.84(9). Symmetry operation: $'-x, y, -z + 1/2$.

The NMR spectroscopic data for the compound are consistent with it retaining its solid state structure in solution, though no signal was observed in its ^{63}Cu NMR spectrum. This presumably results from the quadrupolar nature of this nucleus ($I = 3/2$) and the two isotopes of the gallium center (^{69}Ga , $I = 3/2$, 60.1% abundant; ^{71}Ga , $I = 3/2$, 39.9% abundant) to which it is coordinated. In the solid state, the molecular structure of **6** (Fig. 4) shows it to have three-coordinate Ga and Cu centers, both with distorted trigonal planar geometries. The Cu–Ga distance (2.3054(9) Å) is very close to that in the related copper(I) gallyl, $[(\text{IMes})\text{Cu}\{\text{Ga}(\text{DAB})\}]$ (2.3066(6) Å) [8(g)], despite the fact that the copper center is two-coordinate in that complex.

2.2. Reactivity of metal gallyls towards unsaturated substrates

Considering the wide applicability of transition metal–heterocyclic boryl complexes to synthesis [20], we were interested in investigating the reactivity of the above prepared complexes with unsaturated substrates. All were treated with styrene, phenylacetylene, $\text{Bu}^t\text{N}\equiv\text{C}$, $\text{Bu}^t\text{C}\equiv\text{P}$, CO, CO₂, CS₂ or O₂. Although reactions occurred in most cases, they generated complex product mixtures, the components of which could not be identified.

In light of these discouraging results, attention turned to the further reactivity of a copper gallyl complex previously reported by us, viz. $[(\text{IPr})\text{Cu}\{\text{Ga}(\text{DAB})\}]$ ($\text{IPr} = \text{:C}\{\text{Dip}\}\text{NC}(\text{H})_2$) **7** [8(g)]. Our reasoning for this was that the closely related copper boryl, $[(\text{IPr})\text{Cu}\{\text{B}(\text{pin})\}]$, has been used to great effect as a borylating reagent by Sadighi's group in the past several years [21]. However, despite the similarities between **7** and $[(\text{IPr})\text{Cu}\{\text{B}(\text{pin})\}]$, the former was not found to be effective as a reagent for the gallylation of unsaturated substrates. Saying this, a number of products were isolated from the reaction of **7** with several substrates, as detailed below.

Toluene solutions of compound **7** were found to be unreactive towards ethylene, styrene and but-2-yne. In contrast, a reaction occurred with the terminal alkyne, $\text{PhC}\equiv\text{CH}$, giving the known copper acetylide, **8** [22], in low isolated yield (Scheme 2). It is uncertain what the fate of the gallium heterocycle in this reaction is, but one possibility is that the deprotonation of the alkyne leads to the gallium hydride heterocycle, $[\text{HGa}(\text{DAB})]$, as a by-product. However, no spectroscopic evidence for its presence in the complex mixture of by-products, which included the free DAB ligand, was forthcoming.

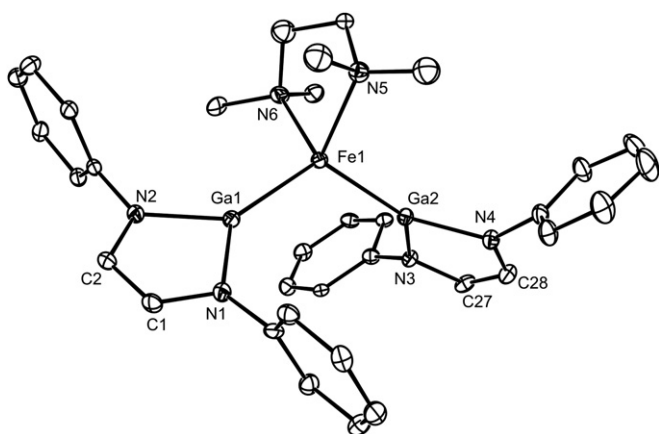


Fig. 2. Molecular structure of **4** (25% probability ellipsoids; hydrogen atoms and isopropyl groups omitted). Selected bond lengths (Å) and angles (°): Ga(1)–N(1) 1.906(7), Ga(1)–N(2) 1.920(6), Ga(1)–Fe(1) 2.5245(14), Ga(2)–N(3) 1.898(7), Ga(2)–N(4) 1.910(7), Ga(2)–Fe(1) 2.5063(14), Fe(1)–N(6) 2.170(7), Fe(1)–N(5) 2.174(8), N(1)–Ga(1)–N(2) 85.3(3), N(3)–Ga(2)–N(4) 85.4(3), Ga(2)–Fe(1)–Ga(1) 122.32(5), N(6)–Fe(1)–N(5) 83.6(3).

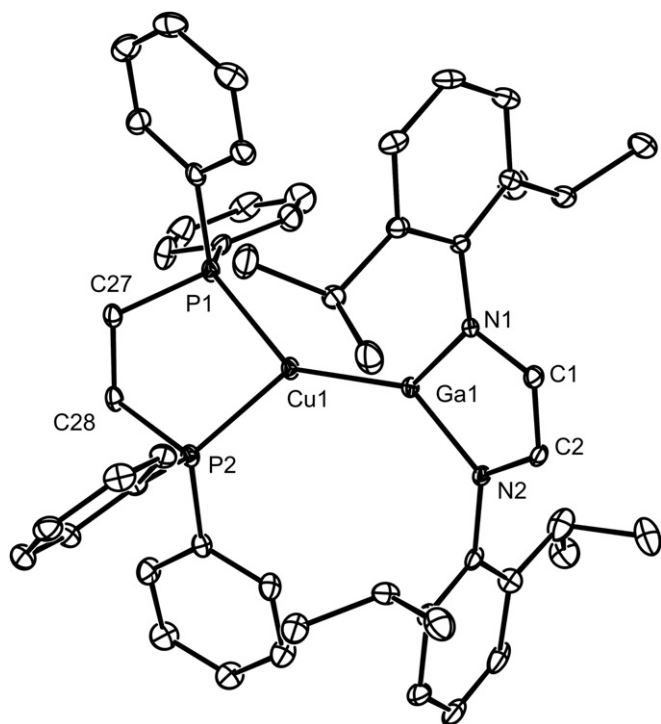
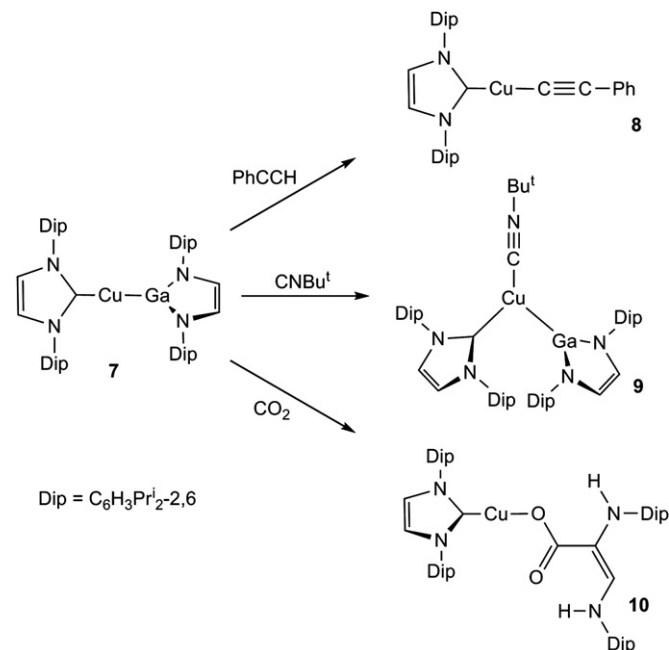


Fig. 4. Molecular structure of **6** (25% probability ellipsoids; hydrogen atoms omitted). Selected bond lengths (Å) and angles ($^{\circ}$): Ga(1)–N(1) 1.898(3), Ga(1)–N(2) 1.901(2), Ga(1)–Cu(1) 2.3054(9), Cu(1)–P(1) 2.2613(10), Cu(1)–P(2) 2.2706(11), N(1)–Ga(1)–N(2) 85.22(11), P(1)–Cu(1)–P(2) 89.90(4), P(1)–Cu(1)–Ga(1) 139.88(3), P(2)–Cu(1)–Ga(1) 127.74(4).

The copper gallyl, **7**, was also found to be unreactive towards PhC(O)H, PhN=NPh, Bu^tNCO, Bu^tNCS and Bu^tC≡P in toluene. It did react with PrⁱN=C=NPrⁱ and 3-buten-2-one, but no single products could be isolated or identified. Conversely, the reaction of **7** with the isonitrile, Bu^tN≡C, led to the isolation of the three-coordinate copper(I) gallyl complex, **9** (Scheme 2). Interestingly, this compound co-crystallizes with **7**, even when it is isolated from a reaction mixture containing an excess of Bu^tN≡C. It seems, therefore, that **9** is in equilibrium with **7** and free Bu^tN≡C in solution, a fact that was confirmed by an NMR spectroscopic analysis of the reaction mixture. These findings are in common with those of Goj et al. from the treatment of [(IPr)CuN(H)Ph] with Bu^tNC [22].

The copper(I) boryl complex, [(IPr)Cu{B(pin)}], has proved effective for the abstraction of oxygen from CO₂, forming [(IPr)Cu{OB(pin)}] and CO. In the presence of excess {B(pin)}₂, this process is catalytic, regenerating [(IPr)Cu{B(pin)}] and forming O{B(pin)}₂ [21(c)]. Theoretical studies suggest that the reaction proceeds *via* an initial insertion of CO₂ into the B–Cu bond [21(d)]. In order to see if similar chemistry could be carried out with **7**, it was treated with an excess of CO₂ in toluene. In contrast to the boryl reaction, the only product isolated from the gallyl reaction was the unusual copper(I) carboxylate, **10** (Scheme 2). Again it is unknown what the mechanism of formation of this complex is, but one possibility is that it involves an initial nucleophilic attack of one DAB backbone carbon of the gallyl ligand of **7** at the carbon center of CO₂. In the presence of adventitious water, concomitant hydrolysis of the gallium heterocycle could occur to give the coordinated carboxylate ligand. It is noteworthy that when the gold analogue of **7**, *viz.* [(IPr)Au{Ga(DAB)}] [8(g)], is exposed to moisture and oxygen, a related transformation of the DAB ligand occurs to yield the gold amide complex, [(IPr)Au{κ¹-N(Dip)C(O)CH₂N(H)Dip}]. Spectroscopic and crystallographic details of this species can be found in the Supplementary Material.



Scheme 2.

The spectroscopic details of **8–10** are compatible with the solid state structures of the compounds which are depicted in Figs. 5–7. The structure of compound **8** has not previously been reported. It is a rare example of a monomeric copper(I) alkynyl complex with a distorted linear geometry at its copper(I) center (C–Cu–C 172.74 (16°)). Both the Cu–C and the C≡C distances are in the normal range for such interactions [17]. As previously eluded to, compound **9** co-crystallizes with one molecule of **7** in the asymmetric unit, though this is not shown in Fig. 6. The copper(I) center of **9** has a distorted trigonal planar coordination geometry, with the relatively obtuse Ga(1)–Cu(1)–C(32) angle ($35.15(13)^{\circ}$) presumably arising from the

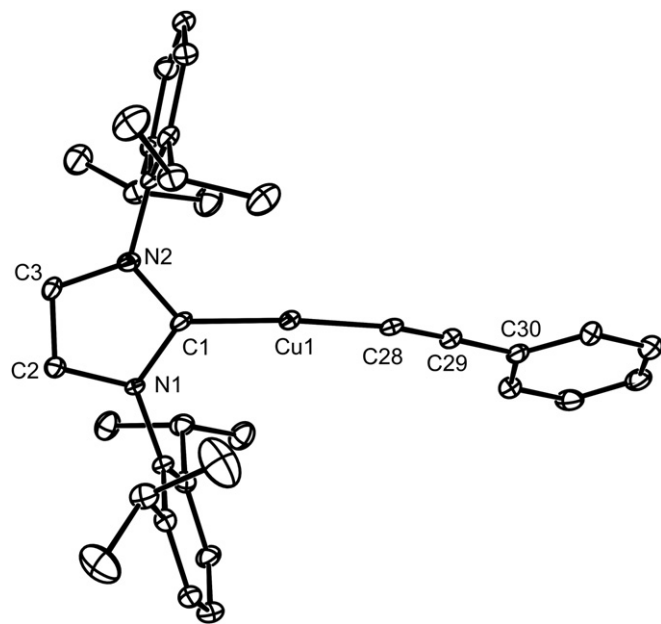


Fig. 5. Molecular structure of **8** (25% probability ellipsoids; hydrogen atoms omitted). Selected bond lengths (Å) and angles ($^{\circ}$): Cu(1)–C(28) 1.861(4), Cu(1)–C(1) 1.890(4), N(1)–C(1) 1.365(5), C(1)–N(2) 1.358(4), C(28)–C(29) 1.209(5), C(28)–Cu(1)–C(1) 172.74 (16), N(2)–C(1)–N(1) 103.5(3).

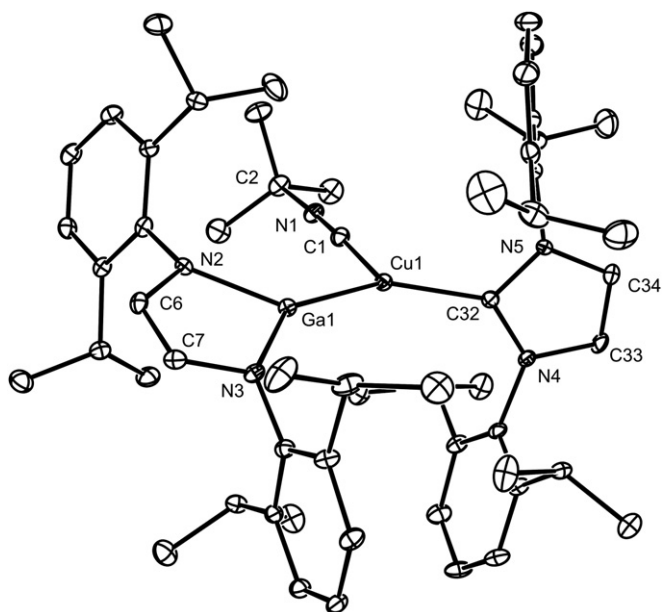


Fig. 6. Molecular structure of **9** (25% probability ellipsoids; hydrogen atoms omitted). Selected bond lengths (Å) and angles ($^{\circ}$): Ga(1)–N(3) 1.926(4), Ga(1)–N(2) 1.940(4), Ga(1)–Cu(1) 2.3707(11), Cu(1)–C(1) 1.935(6), Cu(1)–C(32) 1.968(5), N(1)–C(1) 1.162(6), N(3)–Ga(1)–N(2) 84.74(16), C(1)–Cu(1)–C(32) 115.9(2), C(1)–Cu(1)–Ga(1) 108.95(16), C(32)–Cu(1)–Ga(1) 135.15(13), N(1)–C(1)–Cu(1) 177.6(5).

steric interaction between the two bulky heterocycles. Not surprisingly, the Ga–Cu and C–Cu distances in the complex are longer than those in two-coordinate **7** (2.2807(5) Å and 1.911(2) Å respectively) [**8(g)**], while the $C_{\text{isonitrile}}\text{--Cu}$ separation is the longest reported for a three-coordinate copper(I) complex of $\text{Bu}^t\text{N}\equiv\text{C}$ (cf. 1.900 Å mean in $[\text{ClCu}(\text{C}\equiv\text{NBu}^t)_2]$ [**23**]). The latter observation is in line with the labile nature of the isonitrile ligand in **9**. As was the case for **8**, the copper geometry of **10** is distorted linear, and the Cu–C distances are comparable in both complexes. Interestingly, the CO_2 fragment of

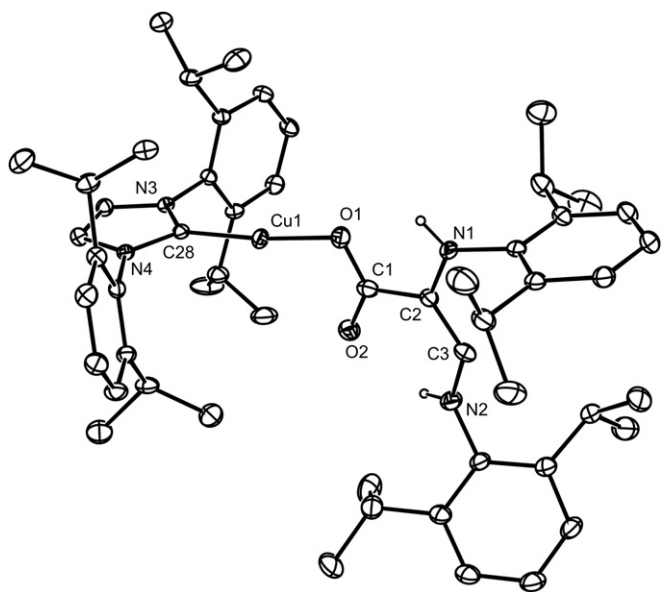


Fig. 7. Molecular structure of **10** (25% probability ellipsoids; non-amine hydrogen atoms omitted). Selected bond lengths (Å) and angles ($^{\circ}$): Cu(1)–C(28) 1.873(4), Cu(1)–O(1) 1.915(3), O(1)–C(1) 1.244(6), N(1)–C(2) 1.396(6), C(1)–O(2) 1.252(6), C(1)–C(2) 1.491(7), N(2)–C(3) 1.372(7), C(2)–C(3) 1.376(7), C(28)–Cu(1)–O(1) 172.61(18), C(1)–O(1)–Cu(1) 109.3(3), O(1)–C(1)–O(2) 126.2(5), C(3)–C(2)–N(1) 120.5(4), N(2)–C(3)–C(2) 126.9(5).

the carboxylate ligand coordinates to the copper center in a $\kappa^1\text{-O}$ fashion, yet its two similar C–O distances suggest delocalization over that fragment. This bonding situation has been observed on several previous occasions for related copper carboxylates, e.g. $[(\text{IPr})\text{Cu}\{\text{OC}(\text{O})\text{CPh}\}]$ [**24**]. An analysis of the bond lengths and angles within the NCCN fragment of the ligand show that it possess a $\text{C}=\text{C}$ double bond and two C–N single bonds. However, as this fragment and the CO_2 unit are essentially co-planar, a degree of conjugation over the ligand backbone is to be expected. There is an intramolecular hydrogen bonding interaction (2.12 Å) between O(2) and the proton attached to N(2).

3. Conclusion

In summary, a series of group 6–9 and 11 metal gallyl complexes have been prepared and, in all but one case, crystallographically characterized. Their treatment with a range of unsaturated substrates has led to either no reaction or complex mixtures of products. The reactivity of a known copper gallyl complex, $[(\text{IPr})\text{Cu}\{\text{Ga}(\text{DAB})\}]$, towards unsaturated substrates has also been explored. Although a number of new complexes have resulted from this study, it is clear that the copper gallyl compound will not prove as useful as have related copper boryls, e.g. $[(\text{IPr})\text{Cu}\{\text{B}(\text{pin})\}]$, for the functionalization of unsaturates.

4. Experimental section

All manipulations were carried out using standard Schlenk and glove box techniques under atmospheres of high purity argon or dinitrogen. THF, hexane and toluene were distilled over potassium, whilst diethyl ether was distilled over Na/K alloy then freeze/thaw degassed prior to use. ^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded on either Bruker DXP300 or DPX400 spectrometers, and were referenced to the residual ^1H or ^{13}C resonances of the solvent used, or 85% external H_3PO_4 ($^{31}\text{P}\{^1\text{H}\}$ NMR). Mass spectra were obtained from the EPSRC National Mass Spectrometry Service at Swansea University. IR spectra were recorded using a Nicolet 510 FT-IR spectrometer as Nujol mulls between NaCl plates. Solution magnetic moments were determined using the Evans method [**25**]. Melting points were determined in sealed glass capillaries under argon, and are uncorrected. Microanalyses were carried out by Campbell Microanalytical, Ottago. $[\text{K}(\text{tmeda})][\text{Ga}(\text{DAB})]$ [**6**], $[\text{CpCr}(\text{IMes})\text{Cl}]$ [**16**], $[\text{MnCl}_2(\text{tmeda})]$ [**26**], $[\text{FeCl}_2(\text{tmeda})_2]$ [**27**], $[\text{CoCl}_2(\text{tmeda})]$ [**26**], $[\{\text{Cu}(\text{dppe})\}_2]$ [**28**] and $[(\text{IPr})\text{Cu}\{\text{Ga}(\text{DAB})\}]$ [**8(g)**] were prepared by variations of literature procedures. All other reagents were used as received.

4.1. $[\text{CpCr}(\text{IMes})\{\text{Ga}(\text{DAB})\}]$ (**2**)

A solution of $[\text{K}(\text{tmeda})][\text{Ga}(\text{DAB})]$ (0.32 g, 0.53 mmol) in THF (10 cm^3) was added to a suspension of $[\text{CpCr}(\text{IMes})\text{Cl}]$ (0.24 g, 0.53 mmol) in THF (10 cm^3) at $-78\text{ }^{\circ}\text{C}$ to give a deep purple solution. The reaction mixture was warmed to $20\text{ }^{\circ}\text{C}$ and stirred overnight. All volatiles were then removed *in vacuo*, the residue washed with hexane (20 cm^3), extracted into diethyl ether (40 cm^3) and filtered. The filtrate was concentrated to ca. 15 cm^3 and stored at $-30\text{ }^{\circ}\text{C}$ to give deep purple blocks of **2**. Further concentration of the supernatant solution gave another crop of **2** (0.33 g, 94%). Mp $105\text{--}110\text{ }^{\circ}\text{C}$ (decomp.); $\mu_{\text{eff}} = 2.45\ \mu\text{B}$; IR ν/cm^{-1} (Nujol): 1671m, 1609m, 1585m, 1557m, 1324m, 1258s, 1110m, 929m, 895m, 854s, 803s, 765s; MS/EI m/z (%): 866 (M^+ , 2), 305 (IMesH^+ , 100).

4.2. $[\text{Mn}(\text{tmeda})\{\text{Ga}(\text{DAB})\}_2]$ (**3**)

To a solution of $[\text{K}(\text{tmeda})][\text{Ga}(\text{DAB})]$ (0.25 g, 0.42 mmol) in THF (20 cm^3) was added a solution of $[\text{MnCl}_2(\text{tmeda})]$ (0.05 g,

0.21 mmol) in THF (20 cm³) at –78 °C. The solution was warmed to room temperature and stirred for one hour to yield a red–green solution. Volatiles were removed *in vacuo*, the residue washed with hexane (15 cm³) and extracted with diethyl ether (40 cm³). Filtration, concentration and cooling to –30 °C overnight yielded red–green crystals of **3** (0.06 g, 27%). Mp 127–129 °C; $\mu_{\text{eff}} = 5.71 \mu_{\text{B}}$; IR ν/cm^{-1} (Nujol): 1580m, 1213s, 1116s, 944s, 897s, 802s, 762s; MS/EI m/z (%): 1063 (M⁺, 4), 446 ((DAB)Ga⁺, 43), 377 (DABH⁺, 80); acc. mass (EI): calc. for C₅₈H₈₈N₆MnGa₂: 1061.4957, found: 1061.4955.

4.3. [Fe(tmeda){Ga(DAB)}₂] (**4**)

A similar procedure to that used to prepare **3**, but using [FeCl₂(tmeda)₂] as the precursor, was employed in the synthesis of green crystalline **4** (yield: 31%). Mp 166–168 °C; $\mu_{\text{eff}} = 5.12 \mu_{\text{B}}$; IR ν/cm^{-1} (Nujol): 1586m, 1259s, 1212s, 1115s, 943s, 800br, 762m, 681m; MS/EI m/z (%): 1064 (M⁺, 6), 446 ((DAB)Ga⁺, 36), 377 (DABH⁺, 100); acc. mass (EI): calc. for C₅₈H₈₈N₆FeGa₂: 1062.4926, found: 1062.4925.

4.4. [Co(tmeda){Ga(DAB)}₂] (**5**)

A similar procedure to that used to prepare **3**, but using [CoCl₂(tmeda)] as the precursor, was employed in the synthesis of red crystalline **5** (yield: 18%). Mp 220–223 °C; $\mu_{\text{eff}} = 2.21 \mu_{\text{B}}$; IR ν/cm^{-1} (Nujol): 1585m, 1252m, 1112s, 804br, 764m, 750; MS/EI m/z (%): 446 ((DAB)Ga⁺, 100), 377 (DABH⁺, 42); anal. calc. for C₅₈H₈₈CoGa₂N₆: C 65.24%, H 8.31%, N 7.87%; found: C 65.01%, H 8.24%, N 7.78%.

4.5. [Cu(dppe){Ga(DAB)}] (**6**)

To a solution of [K(tmeda)][:Ga(DAB)] (0.25 g, 0.42 mmol) in diethyl ether (20 cm³) was added a solution of [(Cu(dppe)I)₂] (0.24 g, 0.21 mmol) in diethyl ether (20 cm³) at –78 °C. The reaction mixture was warmed to room temperature and stirred overnight to yield a red solution. Volatiles were removed *in vacuo*, the residue washed with hexane (20 cm³) and extracted with diethyl ether (30 cm³). Filtration, concentration and cooling to –30 °C overnight yielded red crystals of **6** (0.18 g, 46%). Mp 148–149 °C; ¹H NMR (400 MHz, C₆D₆, 298 K): δ 1.38 (d, ³J_{HH} = 6.9 Hz, 12H, CH(CH₃)₂), 1.56 (d, ³J_{HH} = 6.9 Hz, 12H, CH(CH₃)₂), 1.91 (br. m, 4H, PCH₂), 4.28 (sept, ³J_{HH} = 6.9 Hz, 4H, CH(CH₃)₂), 6.83 (s, 2H, NCH), 7.08–7.48 (m, 26H, Ar-H); ¹³C{¹H} NMR (75 MHz, C₆D₆, 298 K): δ 23.5 (br, PCH₂), 24.0 (CH(CH₃)₂), 25.7 (CH(CH₃)₂), 28.2 (CH(CH₃)₂), 122.8 (NCH), 123.7, 128.5, 128.6, 128.9, 132.8, 146.1 (Ar-C), *ipso*-Cs not observed; ³¹P{¹H} NMR (121 MHz, C₆D₆, 298 K): δ = –3.2 (br); IR ν/cm^{-1} (Nujol): 1585m, 1259s, 1101s, 803m, 761m, 745m, 693m; MS/EI m/z (%): 908 (MH⁺, 2), 446 ((DAB)Ga⁺, 76), 377 (DABH⁺, 24); anal. calc. for C₅₂H₆₀CuGa₂N₂P: C 68.76%, H 6.66%, N 3.08%; found: C 68.09%, H, 6.31%, N 2.99%.}}}

4.6. [(IPr)Cu(C≡CPh)] (**8**)

Phenylacetylene (13 μ l, 0.12 mmol) was added to a solution of [(IPr)Cu{Ga(DAB)}] (0.10 g, 0.11 mmol) in toluene (10 cm³) via a microsyringe at –78 °C to give a yellow solution. The reaction mixture was warmed to 20 °C and stirred overnight. All volatiles

Table 1

Crystal data for compounds **2**, **4–6** and **8–10**.

	2	4 ·(diethyl ether) _{0.5}	5	6
Chemical formula	C ₅₂ H ₆₅ CrGa ₂ N ₄	C ₆₀ H ₉₃ FeGa ₂ N ₆ O _{0.5}	C ₅₈ H ₈₈ CoGa ₂ N ₆	C ₅₂ H ₆₀ CuGa ₂ N ₂ P ₂
Formula weight	867.80	1101.69	1067.71	908.22
T (K)	150(2)	150(2)	150(2)	150(2)
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Triclinic
Space group	<i>Pna</i> 2 ₁	<i>Pbca</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> – 1
<i>a</i> (Å)	29.776(6)	13.991(3)	22.064(4)	12.813(3)
<i>b</i> (Å)	12.217(2)	21.220(4)	12.821(3)	18.090(4)
<i>c</i> (Å)	13.046(3)	46.096(9)	20.430(4)	20.781(4)
α (°)	90	90	90	83.51(3)
β (°)	90	90	105.25(3)	83.60(3)
γ (°)	90	90	90	85.83(3)
<i>V</i> (Å ³)	4745.6(16)	13,685(5)	5575.7(19)	4747.4(17)
<i>Z</i>	4	8	4	4
μ (Mo-K α) (mm ^{–1})	0.834	1.027	1.295	1.118
Reflections collected (<i>R</i> _{int})	51,687 (0.0899)	20,391 (0.0447)	11,352 (0.0622)	36,492 (0.0537)
Unique reflections	10,295	11,818	6029	19,529
<i>R</i> ₁ (<i>I</i> > 2 σ (<i>I</i>))	0.0356	0.1053	0.0435	0.0500
<i>wR</i> ₂ (all data)	0.0904	0.2542	0.0841	0.1109
	8 (toluene)	9 (7)	10	
Chemical formula	C ₄₂ H ₄₉ CuN ₂	C ₁₁₁ H ₁₅₃ Cu ₂ Ga ₂ N ₉	C ₅₄ H ₇₃ CuN ₄ O ₂	
Formula weight	645.37	1879.94	873.70	
T (K)	150(2)	150(2)	150(2)	
Crystal system	Triclinic	Triclinic	Monoclinic	
Space group	<i>P</i> – 1	<i>P</i> – 1	<i>C</i> 2/ <i>c</i>	
<i>a</i> (Å)	12.558(3)	12.668(3)	43.538(9)	
<i>b</i> (Å)	15.065(3)	20.042(4)	10.565(2)	
<i>c</i> (Å)	19.721(4)	22.203(4)	29.248(6)	
α (°)	94.15(3)	99.41(3)	90	
β (°)	93.50(3)	92.96(3)	131.40(3)	
γ (°)	95.99(3)	105.71(3)	90	
<i>V</i> (Å ³)	3692.1(13)	5326.4(18)	10091(3)	
<i>Z</i>	4	2	8	
μ (Mo-K α) (mm ^{–1})	0.621	0.942	0.475	
Reflections collected (<i>R</i> _{int})	22,539 (0.0616)	33,945 (0.0835)	15,873 (0.0534)	
Unique reflections	12,594	18,632	8712	
<i>R</i> ₁ (<i>I</i> > 2 σ (<i>I</i>))	0.0770	0.0751	0.0872	
<i>wR</i> ₂ (all data)	0.2017	0.1287	0.2102	

were then removed *in vacuo*, the residue was washed with hexane (20 cm³), extracted into toluene (20 cm³) and filtered. The filtrate was concentrated to ca. 5 cm³ and stored at –30 °C overnight to give colorless blocks of **8** (0.01 g, 17%). Mp 181–182 °C. Spectroscopic data for **8** have been previously reported [22].

4.7. [(IPr)Cu{Ga(DAB)}(C≡NBu^t)] (**9**)

tert-butylisocyanide (100 μl, 0.88 mmol) was added to a solution of [(IPr)Cu{Ga(DAB)}] (0.15 g, 0.17 mmol) in hexane (20 cm³) via a microsyringe at –78 °C to give an orange solution. The reaction mixture was warmed to 20 °C, stirred for 3 h and filtered. The filtrate was then concentrated to ca. 15 cm³ and stored at –30 °C overnight to give orange blocks of **9** (0.04 g, 13% based on **9**). Mp 40–45 °C (decomp.); ¹H NMR (400 MHz, C₆D₆, 298 K): δ 0.76 (s, 9H, C(CH₃)₃), 1.04 (d, ³J_{HH} = 6.9 Hz, 12H, CH(CH₃)₂), 1.18 (d, ³J_{HH} = 6.9 Hz, 12H, CH(CH₃)₂), 1.40 (d, ³J_{HH} = 6.9 Hz, 12H, CH(CH₃)₂), 1.46 (d, ³J_{HH} = 6.9 Hz, 12H, CH(CH₃)₂), 2.83 (sept, ³J_{HH} = 6.9 Hz, 4H, CH(CH₃)₂), 4.15 (sept, ³J_{HH} = 6.9 Hz, 4H, CH(CH₃)₂), 6.48 (s, 2H, NCH), 6.52 (s, 2H, NCH), 6.90–7.18 (m, 12H, Ar-H); ¹³C{¹H} NMR (75.6 MHz, C₆D₆, 298 K): δ 14.0 (C(CH₃)₃), 24.0, 24.5, 24.7, 26.5 (CH(CH₃)₂), 27.9, 28.5 (CH(CH₃)₂), 31.7 (C(CH₃)₃), 54.8 (CNBu^t), 121.3 (CN), 122.3, 122.6 (Ar-C), 123.4 (CN), 124.2, 134.0, 138.7, 145.5, 145.8, 150.2 (Ar-C), 188.7 (CN₂); IR ν/cm⁻¹ (Nujol): 2148s (C≡N), 1661m, 1587m, 1560m, 1257m, 935m, 872m, 802m; MS (EI 70eV), *m/z* (%): 981 (MH⁺, 3), 446 (Ga(DAB)⁺, 4), 390 (IPrH⁺, 100), 377 (DABH⁺, 6), 333.

N.B. In solution, compound **9** is in equilibrium with **7** and free Bu^tNC. The NMR resonances arising from the latter two species in C₆D₆ solutions were ignored during the assignment of the NMR spectra of **9**.

4.8. [(IPr)Cu{κ¹-OC(O)C(=CNHDip)(NHDip)}] (**10**)

CO₂ gas was bubbled through a solution of [(IPr)Cu{Ga(DAB)}] (0.13 g, 0.15 mmol) in toluene (10 cm³) for 5 min and the flask sealed and stirred overnight. All volatiles were removed *in vacuo*, the residue extracted into hexane (20 cm³) and filtered. The filtrate was concentrated to ca. 10 cm³ and stored at –30 °C overnight to give colorless blocks of **10** (0.02 g, 16%). Mp 183–187 °C (decomp.); ¹H NMR (400 MHz, C₆D₆, 298 K): δ 0.80–1.25 (overlapping d, 48H, CH(CH₃)₂), 2.33 (sept, ³J_{HH} = 6.9 Hz, 4H, CH(CH₃)₂), 3.34 (sept, ³J_{HH} = 6.9 Hz, 2H, CH(CH₃)₂), 3.52 (sept, ³J_{HH} = 6.9 Hz, 2H, CH(CH₃)₂), 6.10 (s, 2H, NCH), 6.35 (s, 1H, NCH), 6.81–7.12 (m, 12H, Ar-H), 9.10 (br., 2H, NH); IR ν/cm⁻¹ (Nujol): 3210br (NH str.), 1720br (CO str.), 1260m, 1093m, 1019m, 801m; MS (EI 70eV), *m/z* (%): 874 (MH⁺, 7), 378 (DABH⁺, 68), 333 (DABH⁺-Prⁱ, 77).

4.9. Crystallographic studies

Crystals of **2**, **4–6** and **8–10** suitable for X-ray crystal 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 F² by full matrix least squares (SHELXL97) [29] using all unique data. Two crystallographically independent molecules of **6** and **8** were refined in the asymmetric units of their respective crystal structures. There are no significant geometric differences between them. Compound **9** co-crystallized with a molecule of [(IPr)Cu{Ga(DAB)}] **7** in the asymmetric unit of the crystal structure. The Flack parameter for the crystal structure of **2** is 0.005(8). Crystal data, details of data collections and refinement are given in Table 1.

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Appendix A. Supplementary material

Full crystallographic details for [(DAB)Ga(Cl)(μ-Me₂NCH₂-)]₂, [(DAB)Ga(OH)(μ-O)]₂ and [(IPr)Au{κ¹-N(Dip)C(O)CH₂N(H)Dip}]; synthetic and spectroscopic details for [(DAB)Ga(OH)(μ-O)]₂ and [(IPr)Au{κ¹-N(Dip)C(O)CH₂N(H)Dip}]. CCDC nos. 776628–776637 contain the supplementary crystallographic data this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www: www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2010.07.016.

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