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Group 9 and 11 Metal(I) Gallyl Complexes Stabilized by N-Heterocyclic Carbene Coordination: First Structural Characterization of Ga−M (M = Cu or Ag) Bonds

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Reactions of the anionic gallium(I) heterocycle $[:Ga\{[N(Ar)C(H)]_2\}]^-$ ($Ar = C_6H_3Pr^i_2$-2,6) with a variety of N-heterocyclic carbene (NHC) complexes of group 9 and 11 halides are reported. In all cases, salt elimination occurs, yielding the neutral metal gallyl complexes $[M(COD)(IMes)\{Ga\{[N(Ar)C(H)]_2\}\}]$ (M = Rh or Ir; COD = 1,5-cyclooctadiene; IMes = $:C\{N(C_6H_2Me_3$-2,4,6$)CH\}_2$) or $[(NHC)M\{Ga\{[N(Ar)C(H)]_2\}\}]$ (M = Cu, Ag, or Au; NHC = IMes, IPr ($:C\{N(Ar)C(H)\}_2$), or ICy ($:C\{N(C_6H_{11})C(Me)\}_2$)). NHC coordination apparently stabilizes the formed complexes toward elimination processes that have been observed in previous studies. The majority of the complexes in this study have been the subjects of X-ray crystallographic studies, which in several cases reveal the first examples of Ga−Cu or Ga−Ag bonds in molecular complexes. Analogies between the gallium heterocycle and cyclic boryl ligands are explored. Solid-state and spectroscopic studies on the prepared complexes suggest that the gallyl ligand has a *trans* influence intermediate between cyclic boryls and chloride.

Introduction

In recent years we have been systematically examining the chemistry of the anionic gallium(I) heterocycle $[:Ga\{[N(Ar)C(H)]_2\}]^-$, **1** ($Ar = C_6H_3Pr^i_2$-2,6), which is a valence isoelectronic analogue of the important N-heterocyclic carbene (NHC) class of ligands. The synthetic versatility of this heterocycle has been amply demonstrated by its use as a ligand in the formation of complexes with metals from across the periodic table.[1] Throughout this work its chemistry has shown similarities to, but also significant differences from, that of NHCs,[2] gallium diyls ($:Ga^IR$),[3] and other neutral gallium(I) heterocycles, e.g., six-membered $[:Ga\{[N(Ar)C(Me)]_2CH\}]$[1,3,4] and four-membered $[:Ga\{[N(Ar)]_2CNCy_2\}]$.[5] Like NHCs, the gallium heterocycle is a strong σ-donor (having a largely sp-hybridized Ga lone pair[6]) and thus readily forms adducts with electron-deficient fragments, e.g., $E\{CH(SiMe_3)_2\}_2$ (E = Ge, Sn,[7] or Mn[8]). In addition, it displaces CO from homo- and heteroleptic transition metal carbonyl complexes to form anionic systems, e.g., $[CpM(CO)_n\{Ga\{[N(Ar)C(H)]_2\}\}]^-$, M = V, Mn, or Co; n = 3, 2, or 1, respectively.[8,9] Moreover, the reducing nature of the gallium(I) center in **1** has seen its use in C−H activation reactions[10] and oxidative insertions into E−E bonds (E = P,[11] Se, or Te[12]), while its carbenoid character has lent it to cycloaddition reactions with unsaturated substrates.[11] It should be noted that, although **1** has an effectively empty p-orbital orthogonal to the heterocycle plane,[6] theoretical studies have suggested it to be a very poor π-acceptor in its transition metal complexes (cf. NHCs).[8]

One area where **1** has not proved as useful as first thought is in salt metathesis reactions with metal halides (MX_n) and their complexes. Until recently these invariably led to paramagnetic gallium(II) dimers, $[GaX\{[N(Ar)C(H)\cdot]_2\}]_2$, X = Cl, Br, or I, presumably via an initial oxidative insertion of the Ga(I) center of **1** into the M−X bond of the metal halide, followed by elimination of the gallium(II) dimer.[13] Saying this, we have successfully effected the elimination of other salts (KH,[14] KCp,[15] or $KCH(SiMe_3)_2$[7]) in metathesis reactions involving a potassium salt of **1**. Of late, the problems associated with reactions of **1** with metal halides have been overcome by coordination of the metal halide with bulky and electron-rich ligands, e.g., NHCs or bulky guanidinates. This has allowed us access to two neutral metal−gallyl complexes containing the first structurally char-

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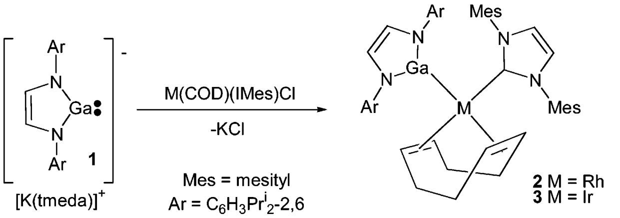
acterized Ga−Sn[7] and Ga−lanthanide[16] bonds in molecular complexes. It seemed to us that this strategy could also lead to a variety of neutral transition metal gallyl complexes [L_nM{Ga{[N(Ar)C(H)]$_2$}}$_m$], which would have parallels with the wide variety of transition metal−cyclic boryl complexes that have been prepared and used as catalysts for a number of synthetic transformations.[17] In this respect it is interesting to note that the direct boron analogue of **1** has been recently described,[18] and its use as a ligand in the formation of transition metal boryls suggested.

The metal boryl most relevant to this study is the structurally characterized copper(I) complex [(IPr)Cu(Bpin)] (IPr = :C{N(Ar)C(H)}$_2$, Bpin = B{OCMe$_2$}$_2$), which is stabilized by NHC coordination and has been reported by Sadighi et al. to borylate alkenes[19] and to catalytically diborylate aldehydes.[20] In addition, it has been shown to be an effective catalyst in the reduction of CO_2 to CO.[21] It is of note that there are no structurally characterized examples of cyclic boryl complexes of the other group 11 metals, silver, or gold. Boryl complexes of the group 9 metals are, however, more prevalent, and a number of catecholato- and pinacolatoboryl complexes of Co, Rh and Ir have been described.[17] Examples of these have been widely utilized for, or suggested as intermediates in, the catalytic borylation or hydroboration of unsaturated compounds and the C−H activation of alkanes, arenes, and heteroarenes.[17] Despite this, no structurally characterized NHC-coordinated group 9 metal boryl complexes have yet been reported. In this study we detail successful salt metathesis reactions between **1** and NHC-coordinated group 9 or 11 halide fragments that have given rise to a variety of metal gallyl complexes, examples of which exhibit the first structurally authenticated Cu−Ga and Ag−Ga bonds in molecular complexes. These complexes hold potential for use in synthetic transformations related to those effected by metal boryl complexes.

Results and Discussion

Group 9 Chemistry. Our previous work with **1** has shown that it can readily reduce transition metal fragments to lower accessible oxidation states.[22] As a result, all attempts to form group 9 metal gallyl complexes involved metal(I) halide precursors. In early work, a potassium salt of the gallyl anion [K(tmeda)][**1**] was reacted with either [M(COD)Cl]$_2$ (M = Rh or Ir, COD = 1,5-cyclooctadiene), [MCl(PPh$_3$)$_3$] (M = Co or Rh), or [Ir(CO)Cl(PPh$_3$)$_2$]. In all cases, the gallium(II) dimer [GaCl{[N(Ar)C(H)$^\bullet$]$_2$}]$_2$ was the only identifiable product. As previously mentioned, it is believed that this occurs via an initial oxidative insertion of the Ga(I) center of **1** into the M−Cl bond of the transition metal precursor, followed by further decomposition. In this respect, it is worthy of mention that the related neutral six-membered heterocycle [:Ga{[N(Ar)C(Me)]$_2$CH}] has been shown to insert into Rh−Cl bonds.[23] Considering that coordination of f-block metal halides with NHCs can circumvent such insertions in their reactions with **1**,[16] an extension of this methodology to group 9 metals was explored.

Scheme 1



Treatment of [M(COD)(IMes)Cl] (M = Rh or Ir, IMes = :C{N(C$_6$H$_2$Me$_3$-2,4,6)CH}$_2$) with 1 equiv of [K(tmeda)][**1**] yielded complexes **2** and **3**, respectively, in moderate to high yields (Scheme 1). Addition of a further equivalent of [K(tmeda)][**1**] to **2** or **3** gave no reaction. Both complexes are air sensitive but indefinitely stable at ambient temperature under argon. It, therefore, seems that IMes coordination of the group 9 metal halide precursor effectively protects the metal center from reduction by **1**, presumably because of the donor strength and steric bulk of the NHC ligand.

The NMR spectroscopic data for **2** and **3** are consistent with their proposed formulations, although no signal was observed in the ^{103}Rh NMR spectrum of **2**. This is probably a result of the coordination of its rhodium center by quadrupolar gallium (^{69}Ga, 60.1%, $I = 3/2$; ^{71}Ga, 39.9%, $I = 3/2$). A $^1J_{\mathrm{RhC}}$ coupling of 52.0 Hz to the IMes carbene center was observed in the ^{13}C{^{1}H} NMR spectrum of **2**, which is similar to that in the precursor molecule [Rh(COD)(IMes)Cl] ($^1J_{\mathrm{RhC}} = 51.9$ Hz).[24] It is of interest that both $^1J_{\mathrm{RhC}}$ couplings to the alkenic carbons of the COD ligand of **2** (7.0 and 8.0 Hz) are significantly less than that corresponding to the carbons *trans* to the chloride ligand of [Rh(COD)(IMes)Cl] ($^1J_{\mathrm{RhC}} = 14.5$ Hz; n.b., the $^1J_{\mathrm{RhC}}$ coupling for the carbons *trans* to IMes is 7.6 Hz). This suggests that **1** has a greater *trans* influence than the chloride ligand, a proposal for which there is crystallographic evidence (*vide infra*).

Compounds **2** and **3** are isostructural, so only the molecular structure of **2** is depicted in Figure 1 (relevant geometric parameters for **3** are included in the caption). Both compounds are monomeric and possess distorted square-planar group 9 metal centers with their IMes and gallyl ligands *cis* to each other. The geometries of the gallyl ligands are similar to each other and to those of previously reported transition metal complexes of **1**.[1] A survey of the Cambridge Crystallographic Database revealed that the Ga−Rh distance in **2** is in the known range (2.33−2.63 Å),[25] while there has only been one previously structurally characterized Ga−Ir bond in [Ir{Ga(Me)$_2$N(SiMe$_2$CH$_2$PPh$_2$)$_2$}{C(=CH$_2$)(Me)}], which at 2.4480(7) Å[26] is considerably shorter than that in **3**.

Evidence for the aforementioned greater *trans* influence of **1** compared to chloride comes from the significantly greater

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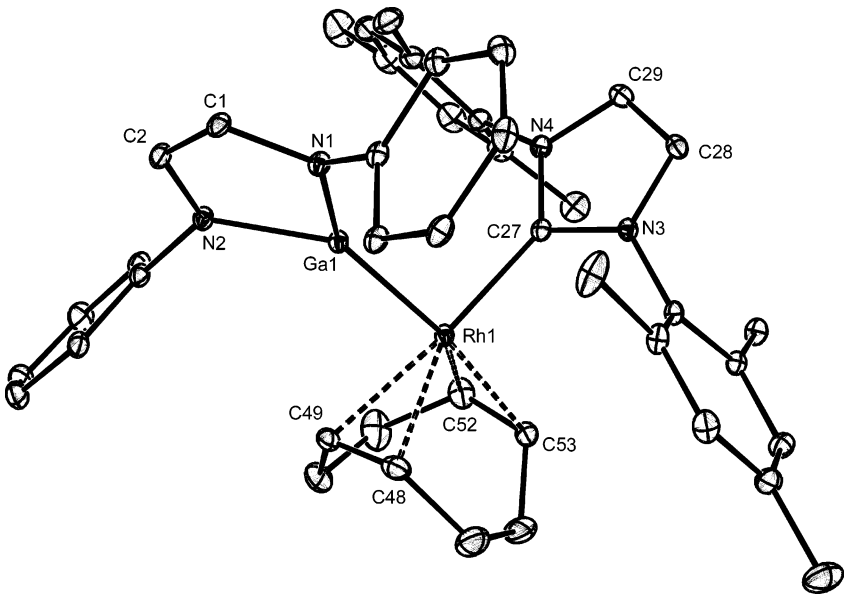
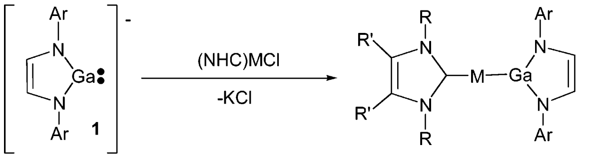


Figure 1. Thermal ellipsoid plot (25% probability surface) of the molecular structure of [Rh(COD)(IMes){Ga{[N(Ar)C(H)]$_2$}}] (**2**). Hydrogen atoms and isopropyl groups are omitted for clarity. Selected bond lengths (Å) and angles (deg): Rh(1)−C(27) 2.059(2), Rh(1)−C(48) 2.165(3), Rh(1)−C(52) 2.193(3), Rh(1)−C(49) 2.224(3), Rh(1)−C(53) 2.243(2), Rh(1)−Ga(1) 2.4259(6), Ga(1)−N(1) 1.913(2), Ga(1)−N(2) 1.926(2), N(1)−C(1) 1.407(3), C(1)−C(2) 1.341(4), N(2)−C(2) 1.395(3), C(48)−C(49) 1.371(4), C(52)−C(53) 1.374(4), C(27)−Rh(1)−Ga(1) 93.08(7), N(1)−Ga(1)−N(2) 86.03(9), N(4)−C(27)−N(3) 102.5(2). Selected bond lengths (Å) and angles (deg) for **3**: Ir(1)−C(27) 2.039(2), Ir(1)−C(53) 2.155(2), Ir(1)−C(49) 2.164(2), Ir(1)−C(52) 2.204(2), Ir(1)−C(48) 2.232(2), Ir(1)−Ga(1) 2.4689(5), Ga(1)−N(2) 1.9198(19), Ga(1)−N(1) 1.9274(19), N(1)−C(1) 1.399(3), N(2)−C(2) 1.399(3), C(1)−C(2) 1.340(3), C(48)−C(49) 1.394(4), C(52)−C(53) 1.394(4), C(27)−Ir(1)−Ga(1) 96.23(6), N(2)−Ga(1)−N(1) 85.69(8), N(4)−C(27)−N(3) 103.24(18).

Scheme 2



4 M = Cu, R = Mes, R' = H
5 M = Ag, R = Mes, R' = H
6 M = Au, R = Mes, R' = H
7 M = Cu, R = Ar, R' = H
8 M = Ag, R = Ar, R' = H
9 M = Au, R = Ar, R' = H
10 M = Cu, R = C_6H_{11}, R' = Me

Rh−C$_{alkene}$ distances in **2** (2.22 Å mean, *trans* to Ga) compared to those in [Rh(COD)(IMes)Cl] (2.11 Å mean, *trans* to Cl[24]). In contrast, the Rh−C$_{alkene}$ separations for the alkene fragment *trans* to IMes are similar in both compounds (**2**: 2.19 Å mean; [Rh(COD)(IMes)Cl]: 2.20 Å mean). Moreover, the Rh−C$_{carbene}$ distance in **2** is close to that in [Rh(COD)(IMes)Cl] (2.0494(16) Å). A comparison of the cyclooctadiene C═C distance *trans* to Cl in [Rh(COD)(IMes)Cl] (1.408(3) Å) with that *trans* to the gallyl ligand of **2** (1.374(4) Å) is in accord with the proposed greater *trans* influence of **1** over chloride. An argument could also be made that the similarities between the two cyclooctadiene C═C distances in **2** point toward a similar *trans* influence for its gallyl and NHC ligands. Comparisons between **3** and [Ir(COD)(IMes)Cl] cannot be carried out, as the latter has not been structurally characterized.

Group 11 Chemistry. In consideration of the stability of **2** and **3**, the 1:1 reactions of **1** with a series of NHC complexes of group 11 metal(I) halides, [(NHC)MCl] (M = Cu, Ag or Au; NHC = IMes or IPr), were carried out. In each case, the salt metathesis product, [(NHC)M{Ga{[N(Ar)C(H)]$_2$}}] (**4**−**9**), was obtained in moderate to high yield (NHC = IPr) or low to moderate yield (NHC = IMes) (Scheme 2). During the course of all reactions, deposition of some elemental group 9 metal was observed upon warming the mixtures from −78 °C to 20 °C. However, once formed, the products were found to be stable in solution at ambient temperature for days. On one occasion, prolonged storage (ca. 2 weeks) of a hexane solution of **9** led to deposition of several yellow crystals of the salt [Au(IPr)$_2$][Ga{[N(Ar)C(H)]$_2$}$_2$]. This is presumably formed via the partial decomposition of **9**. No data on the compound were obtained due to its low yield, although details of its crystal structure are included in the Supporting Information. More metal deposition was observed in reactions involving [(IMes)MCl], which suggests that the greater steric bulk of IPr over IMes contributes to the greater yields of **7**−**9** compared to **4**−**6**. The importance of the steric bulk of the NHC in these syntheses was further tested in the reaction of **1** with [(ICy)CuCl] (ICy = :C{N(C_6H_{11})C(Me)}$_2$), which incorporates a smaller NHC. Despite this, a moderate yield of **10** resulted (Scheme 2). In addition, the complex has a thermal stability in the solid state similar to that of **4**. The higher than expected yield and stability of **10** can perhaps be explained by the greater donor strength of ICy over IMes,[27] which gives the smaller ligand an ability to stabilize copper gallyl fragments similar to that of the larger NHC.

The ^{1}H and ^{13}C{^{1}H} NMR spectroscopic data for **4**−**10** reflect their proposed monomeric structures and will not be commented on here, except to say that the carbene resonances in the ^{13}C{^{1}H} NMR spectra of the silver and gold gallyl complexes were not observed. In addition, no signals were seen in the ^{109}Ag NMR spectra of **5** and **8**. As was the case for **2**, the latter observation can be explained by broadening of these peaks by the adjacent quadrupolar gallium center to a point where they are indistinguishable from the baseline noise. Signals due to molecular ions exhibiting the expected isotopic distribution patterns are present in the EI mass spectra of all complexes.

The X-ray crystal structures of **4**−**8** were obtained and show all to have similar distorted linear group 11 metal geometries.

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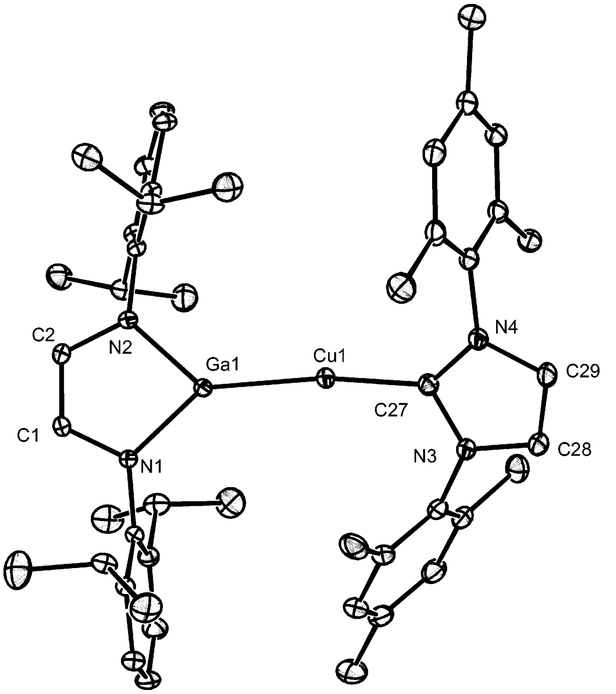

Figure 2. Thermal ellipsoid plot (25% probability surface) of the molecular structure of $[(\mathrm{IMes})\mathrm{Cu}\{\mathrm{Ga}\{[\mathrm{N(Ar)C(H)}]_2\}\}]$ (**4**). Hydrogen atoms are omitted for clarity.

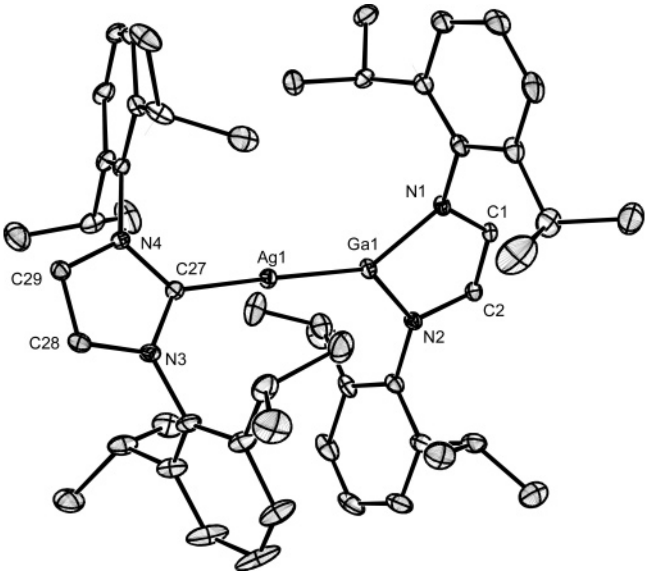

Figure 3. Thermal ellipsoid plot (25% probability surface) of the molecular structure of $[(\mathrm{IPr})\mathrm{Ag}\{\mathrm{Ga}\{[\mathrm{N(Ar)C(H)}]_2\}\}]$ (**8**). Hydrogen atoms are omitted for clarity.

Accordingly, only two representative molecular structures (those of **4** and **8**) are depicted in Figures 2 and 3. A comparison of relevant geometrical parameters of the complexes is included in Table 1. The geometries of the heterocyclic ligands in the complexes are similar to each other and to the majority of previously reported complexes incorporating them.[1,2] In no complex do the gallyl and NHC heterocycles approach coplanarity, as the angles between their least-squares planes vary from 25.3° to 44.9° in the series. There have been no previously reported examples of structurally characterized Ga−Cu or Ga−Ag bonds in molecular compounds, so comparisons cannot be made with the M−Ga distances in **4**, **5**, **7**, and **8**. The Ga−Au distance in **6** is, however, at the low end of the known range (2.377−2.620 Å) for the four previously reported Ga−Au bonded complexes.[28]

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 4−8

	4	**5**	**6**	**7**	**8**
Ga−M	2.3066(6)	2.4161(5)	2.3782(6)	2.2807(5)	2.4108(8)
C−M	1.924(3)	2.125(2)	2.053(4)	1.911(2)	2.120(4)
N−Ga	1.904(2)	1.8897(17)	1.881(3)	1.891(2)	1.898(3)
	1.897(2)	1.8916(18)	1.887(3)	1.891(2)	1.900(3)
N−$\mathrm{C_{carbene}}$	1.359(4)	1.359(3)	1.360(5)	1.354(3)	1.357(5)
	1.363(4)	1.351(3)	1.341(5)	1.358(3)	1.359(5)
Ga−M−C	170.72(8)	165.85(6)	174.06(11)	177.14(7)	178.73(11)
N−Ga−N	85.36(9)	85.41(7)	86.27(14)	85.59(9)	85.89(15)
N−C−N	103.6(2)	104.07(17)	104.8(3)	104.1(2)	103.9(3)

The characterization of the isostructural series **4**−**6** does allow comparisons of the M−Ga bonds in these compounds. Not suprisingly, the Cu−Ga interaction in **4** is the shortest, but interestingly, the Ag−Ga distance in **5** is significantly larger (by ca. 0.04 Å) than the Au−Ga separation in **6**. In addition, the C−Ag bond in **5** is longer than the C−Au bond in **6** by ca. 0.08 Å. In this respect, the relative sizes of gold and silver have been the subject of a study by Schmidbaur *et al*. using a pair of isomorphic complexes, $[\mathrm{M(PMes_3)_2}][\mathrm{BF_4}]$ (M = Au, Ag; Mes = mesityl).[29] In contrast to the values usually quoted for the ionic or covalent radii of Au(I) and Ag(I), where silver is smaller or equal in size to gold,[30] the data from the structures of this pair indicated that the M−P distance is smaller for M = Au by 0.09 Å.

Another structural comparison can be made between the IPr-coordinated copper gallyl complex **7** and the previously reported boryl complex [(IPr)Cu(Bpin)].[21] The C−Cu bond in the former is significantly shorter than that of the latter (1.937(2) Å), despite the gallyl ligand being considerably more bulky than the boryl, Bpin. In addition, the C−Cu distance in [(IPr)CuCl] (1.881(7) Å)[31] is shorter than in the other two complexes. In combination with the results from the group 9 studies, we propose that these observations suggest the gallyl ligand to have a weaker *trans* influence than the boryl,[32] but a stronger *trans* influence than chloride.

Conclusions

In summary, the ability of the gallyl anion $[:\mathrm{Ga}\{[\mathrm{N(Ar)C(H)}]_2\}]^-$, **1**, to participate in salt metathesis reactions with a range of NHC-coordinated group 9 and 11 metal chloride complexes has been demonstrated. The NHC ligands appear to play a vital role in the stabilization of the formed complexes and/or reaction intermediates toward elimination processes. This has allowed access to a variety of group 9 and 11 metal(I) gallyl complexes, examples of which exhibit the first structurally characterized Cu−Ga or Ag−Ga bonds in molecular complexes. In these neutral complexes, analogies have been drawn between **1** and cyclic boryl ligands, complexes of which are widely used in organic transformations. Furthermore, a scale of *trans* influences has been tentatively established for the series $\mathrm{Cl}^- <$ **1** < boryl. Considering the wide synthetic use of group 9 and

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11 metal boryl complexes, there is much potential in this area for gallyl complexes of these metals. Perhaps the greatest potential lies with complexes of the type [(NHC)Cu{Ga{[N(Ar)C(H)]$_2$}}] (**4**, **7**, and **10**), which are closely related to copper boryls, e.g., [(NHC)Cu(Bpin)], which have been used to great effect as borylating reagents by Sadighi's group in recent years. We are currently exploring this potential and will report on it in due course.

Experimental Section

General Methods. All manipulations were carried out using standard Schlenk and glovebox techniques under an atmosphere of high-purity argon. THF and hexane were distilled over potassium, while diethyl ether was distilled over Na/K alloy. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on either a Bruker DPX400 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. Mass spectra were obtained from the EPSRC National Mass Spectrometric Service at Swansea University. IR spectra were recorded using a Nicolet 510 FT-IR spectrometer as Nujol mulls between NaCl plates. Microanalyses were carried out by Medac Ltd. A reproducible microanalysis of **6** was not obtained, but the ^{1}H NMR spectrum of the compound shows it to have a purity of >95% (see Supporting Information). Melting points were determined in sealed glass capillaries under argon and are uncorrected. The compounds [K(tmeda)][**1**];[33] [M(COD)(IMes)Cl], M = Rh[24] or Ir;[34] [(IMes)MCl], M = Cu,[35] Ag,[36] or Au;[37] and [(IPr)MCl], M = Cu,[31] Ag,[38] or Au[39] were synthesized by literature procedures. [(ICy)CuCl] was prepared by a variation of a literature procedure.[35] All other reagents were used as received.

Preparation of [Rh(COD)(IMes){Ga{[N(Ar)C(H)]$_2$}}] (2). A solution of [K(tmeda)][:Ga{[N(Ar)C(H)]$_2$}] (0.21 g, 0.35 mmol) in diethyl ether (20 cm^3) was added to a solution of [Rh(COD)(IMes)Cl] (0.19 g, 0.35 mmol) in diethyl ether (10 cm^3) at −78 °C to give a deep red-orange solution. The reaction mixture was warmed to 20 °C and stirred for 3 h. All volatiles were then removed *in vacuo*, and the residue was extracted into hexane (60 cm^3) and filtered. The filtrate was concentrated to ca. 50 cm^3 and stored at −30 °C overnight to give deep orange rods of **2** (0.21 g, 65%). Mp: 85−86 °C (dec). ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ 1.30−1.92 (m, 8 H, CH_2CH), 1.35 (br m, 12 H, (CH_3)$_2$CH), 1.60 (br m, 12 H, (CH_3)$_2$CH), 1.81 (br s, 6 H, *p*-CH_3), 2.23 (br s 12 H, *o*-CH_3), 3.57 (br m, 2 H, C*H*(CH$_3$)$_2$), 4.01 (br m, 2 H, C*H*(CH$_3$)$_2$), 4.29 (m, 2 H, C*H*CH$_2$), 5.04 (m, 2 H, C*H*CH$_2$), 6.11 (s, 2 H, NC*H*), 6.48 (s, 2 H, NC*H*), 6.74−7.40 (m, 10 H, Ar-*H*). ^{13}C{^{1}H} NMR (75.6 MHz, C_6D_6, 298 K): δ 17.8 (*p*-CH$_3$), 19.5, 20.7 (*o*-CH$_3$), 22.8, 23.8, 26.2, 27.2 (CH(*C*H$_3$)$_2$), 27.9, 28.0 (*C*H(CH$_3$)$_2$), 31.7, 31.9 (*C*H$_2$CH), 80.6 (d, $^{1}J_{RhC}$ = 7.0 Hz, *C*HCH$_2$), 83.9 (d, $^{1}J_{RhC}$ = 8.0 Hz, *C*HCH$_2$), 122.6, 123.1 (H*C*N), 123.9, 124.0, 128.6, 129.8, 130.0, 134.7, 136.6, 136.8, 138.3, 144.3, 146.4, 149.9 (Ar-*C*), 190.9 (d, $^{1}J_{RhC}$ = 52.0 Hz, *C*N$_2$). IR ν/cm^{-1} (Nujol): 1659 m, 1609 m, 1588 m, 1352 m, 1317 m, 1254 m, 852 m. MS (EI 70 eV), *m/z* (%): 854 (MH$^+$ − COD, 10), 516 ((COD)Rh(IMes)H$^+$, 13), 407 (Rh(IMes)H$^+$, 5), 378 ({N(Ar)C(H)}$_2$H$^+$, 8), 305 (IMesH$^+$, 43). $C_{55}H_{72}N_4GaRh$ requires C 68.68, H 7.55, N 5.83, found C 67.93, H 7.94, N 5.24.

Preparation of [Ir(COD)(IMes){Ga{[N(Ar)C(H)]$_2$}}] (3). A solution of [K(tmeda)][:Ga{[N(Ar)C(H)]$_2$}] (0.19 g, 0.31 mmol) in diethyl ether (20 cm^3) was added to a solution of [Ir(COD)(IMes)Cl] (0.20 g, 0.31 mmol) in diethyl ether (10 cm^3) at −78 °C to give a deep purple solution. The reaction mixture was warmed to 20 °C and stirred for 3 h. Volatiles were then removed *in vacuo*, and the residue was extracted into hexane (60 cm^3) and filtered. The filtrate was concentrated to ca. 15 cm^3 and stored at −30 °C overnight to give deep purple blocks of **3** (0.19 g, 51%). Mp: 157−159 °C (dec). ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ 1.35−2.20 (m, 8 H, CH_2CH), 1.43 (d, $^{3}J_{HH}$ = 6.9 Hz, 6 H, (CH_3)$_2$CH), 1.45 (d, $^{3}J_{HH}$ = 6.9 Hz, 6 H, (CH_3)$_2$CH), 1.58 (d, $^{3}J_{HH}$ = 6.9 Hz, 6 H, (CH_3)$_2$CH), 1.61 (d, $^{3}J_{HH}$ = 6.9 Hz, 6 H, (CH_3)$_2$CH), 2.10 (s, 6 H, *p*-CH_3), 2.22 (br s, 12 H, *o*-CH_3), 3.78 (br m, 2 H, C*H*CH$_2$), 4.08 (sept, $^{3}J_{HH}$ = 6.9 Hz, 2 H, C*H*(CH$_3$)$_2$), 4.12, (sept, $^{3}J_{HH}$ = 6.9 Hz, 2 H, C*H*(CH$_3$)$_2$), 4.72 (br m, 2 H, C*H*CH$_2$), 6.10 (br s, 2 H, NC*H*), 6.55 (br s, 2 H, NC*H*), 6.71−7.39 (m, 10 H, Ar-*H*). ^{13}C{^{1}H} NMR (75.6 MHz, C_6D_6, 298 K): δ 17.8, 19.5 (*o*-CH$_3$), 20.7 (*p*-CH$_3$) 23.2, 23.4, 26.7, 26.8 (CH(*C*H$_3$)$_2$), 27.9, 28.4 (*C*H(CH$_3$)$_2$), 31.7, 32.9 (*C*H$_2$CH), 67.8, 68.5 (*C*HCH$_2$), 122.4, 124.5 (br, H*C*N), 122.8, 123.0, 124.0, 128.6, 129.7, 134.4, 134.7, 136.7, 138.5, 146.1, 146.2, 149.7 (Ar-*C*), 185.8 (br, *C*N$_2$). MS (EI 70 eV), *m/z* (%): 602 ((COD)Ir(IMes)H$^+$, 42), 496 (Ir(IMes)H$^+$, 72), 305 (IMesH$^+$, 55). IR ν/cm^{-1} (Nujol): 1658 m, 1608 m, 1588 m, 1355 m, 1316 m, 1254 m, 851 m. EI acc mass: on M$^+$: calc for $C_{55}H_{72}N_4Ga^{191}Ir$ 1048.4613, found 1048.4609. $C_{55}H_{72}N_4GaIr$ requires C 62.85, H 6.90, N 5.33; found C 62.71, H 7.05, N 5.22.

Preparation of [(IMes)Cu{Ga{[N(Ar)C(H)]$_2$}}] (4). A solution of [K(tmeda)][:Ga{[N(Ar)C(H)]$_2$}] (0.24 g, 0.40 mmol) in THF (10 cm^3) was added to a suspension of [(IMes)CuCl] (0.16 g, 0.40 mmol) in THF (10 cm^3) at −78 °C to give a yellow solution. The reaction mixture was warmed to 20 °C and stirred overnight. Volatiles were then removed *in vacuo*, and the residue was extracted into hexane (40 cm^3) and filtered. The filtrate was concentrated to ca. 15 cm^3 and stored at −30 °C overnight to give yellow blocks of **4** (0.12 g, 37%). Mp: 149−152 °C (dec). ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ 1.26 (d, $^{3}J_{HH}$ = 6.9 Hz, 12 H, (CH_3)$_2$CH), 1.47 (d, $^{3}J_{HH}$ = 6.9 Hz, 12 H, (CH_3)$_2$CH), 1.87 (s, 12 H, *o*-CH_3), 2.20 (s, 6 H, *p*-CH_3), 3.90 (sept, $^{3}J_{HH}$ = 6.9 Hz, 4 H, C*H*(CH$_3$)$_2$), 5.94 (s, 2 H, NC*H*), 6.57 (s, 2 H, NC*H*), 6.76 (s, 4 H, Ar-*H IMes*), 7.05−7.35 (m, 6 H, Ar-*H*). ^{13}C{^{1}H} NMR (75.6 MHz, C_6D_6, 298 K): δ 17.3 (*o*-*C*H$_3$), 20.9 (*p*-*C*H$_3$) 24.6, 26.0 (CH(*C*H$_3$)$_2$), 27.7 (*C*H(CH$_3$)$_2$), 121.1, 123.7 (H*C*N), 121.6, 122.4, 129.3, 134.2, 134.9, 138.8, 145.7, 147.8 (Ar-*C*), 181.2 (br, *C*N$_2$). MS (EI 70 eV), *m/z* (%): 814 (MH$^+$, 3), 378 ({N(Ar)C(H)}$_2$H$^+$, 100). IR ν/cm^{-1} (Nujol): 1656 m, 1586 m, 1549 m, 1357 m, 1321 m, 1259 m, 1113 m, 851 m, 806 m. EI acc mass: on M$^+$: calc for $C_{47}H_{60}N_4CuGa$ 812.3364, found 812.3372. $C_{47}H_{60}N_4CuGa$ requires C 69.33, H 7.43, N 6.88; found C 69.25, H 7.53, N 7.01.

Preparation of [(IMes)Ag{Ga{[N(Ar)C(H)]$_2$}}] (5). A solution of [K(tmeda)][:Ga{[N(Ar)C(H)]$_2$}] (0.27 g, 0.45 mmol) in THF (15 cm^3) was added to a suspension of [(IMes)AgCl] (0.20 g, 0.45 mmol) in THF (15 cm^3) at −78 °C to give a deep yellow solution. The reaction mixture was warmed to 20 °C and stirred overnight. Volatiles were removed *in vacuo*, and the residue was extracted into hexane (40 cm^3) and filtered. The filtrate was concentrated to ca. 15 cm^3 and stored at −30 °C to give yellow blocks of **5** (0.05 g, 13%). Mp: 105−109 °C (dec). ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ 1.30 (d, $^{3}J_{HH}$ = 6.9 Hz, 12 H, (CH_3)$_2$CH), 1.48 (d, $^{3}J_{HH}$ = 6.9 Hz, 12 H, (CH_3)$_2$CH), 1.86 (s, 12 H, *o*-CH_3), 2.27 (s, 6 H, *p*-CH_3), 3.95 (sept, $^{3}J_{HH}$ = 6.9 Hz, 4 H, C*H*(CH$_3$)$_2$), 6.07 (s, 2 H, NC*H*), 6.60 (s, 2 H, NC*H*), 6.76 (s, 4 H, Ar-*H IMes*), 7.17−7.37 (m, 6 H, Ar-*H*). ^{13}C{^{1}H} NMR (75.6 MHz, C_6D_6, 298 K): δ 17.2 (*o*-*C*H$_3$), 20.8 (*p*-CH$_3$) 24.5, 26.0 (CH(*C*H$_3$)$_2$), 27.7 (*C*H(CH$_3$)$_2$),

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121.4, 123.8 (HCN), 121.7, 122.4, 129.3, 134.3, 135.4, 138.8, 145.8, 147.5 (Ar-*C*), *C*N$_2$ not observed. MS (EI 70 eV), *m/z* (%): 858 (M$^+$, 1), 378 ({N(Ar)C(H)}$_2$H$^+$, 28). IR ν/cm^{-1} (Nujol): 1607 m, 1587 m, 1578 m, 1546 m, 1357 m, 1264 m, 1115 m, 852 m. EI acc mass: on M$^+$: calc for $C_{47}H_{60}N_4AgGa$ 856.3119, found 856.3123. $C_{47}H_{60}N_4AgGa$ requires C 65.75, H 7.04, N 6.52; found C 65.75, H 7.43, N 6.29.

Preparation of [(IMes)Au{Ga{[N(Ar)C(H)]$_2$}}] (6). A solution of [K(tmeda)][:Ga{[N(Ar)C(H)]$_2$}] (0.21 g, 0.35 mmol) in THF (10 cm^3) was added to a suspension of [(IMes)AuCl] (0.19 g, 0.35 mmol) in THF (10 cm^3) at −78 °C to give a yellow solution. The reaction mixture was warmed to 20 °C and stirred overnight. Volatiles were removed *in vacuo*, and the residue was extracted into hexane (30 cm^3) and filtered. The filtrate was concentrated to ca. 15 cm^3 and stored at −30 °C for 48 h to give yellow blocks of **6** (0.04 g, 12%). Mp: 104−108 °C (dec). ^{1}H NMR (400 MHz, C$_6$D$_6$, 298 K): δ 1.46 (d, $^3J_{HH}$ = 6.9 Hz, 12 H, (C*H*$_3$)$_2$CH), 1.63 (d, $^3J_{HH}$ = 6.9 Hz, 12 H, (C*H*$_3$)$_2$CH), 2.04 (s, 12 H, *o*-C*H*$_3$), 2.46 (s, 6 H, *p*-C*H*$_3$), 4.05 (sept, $^3J_{HH}$ = 6.9 Hz, 4 H, C*H*(CH$_3$)$_2$), 6.15 (s, 2 H, NC*H*), 6.73 (s, 2 H, NC*H*), 6.91 (s, 4 H, Ar-*H IMes*), 7.39−7.51 (m, 6 H, Ar-*H*). ^{13}C{^{1}H} NMR (75.6 MHz, C$_6$D$_6$, 298 K): δ 17.2 (*o*-CH$_3$), 20.9 (*p*-CH$_3$) 24.4, 26.0 (CH(*C*H$_3$)$_2$), 27.7 (*C*H(CH$_3$)$_2$), 121.2, 124.1, (HCN), 121.3, 122.5, 129.2, 134.3, 134.7, 138.9, 145.9, 146.9 (Ar-*C*), *C*N$_2$ not observed. MS (EI 70 eV), *m/z* (%): 946 (M$^+$, 10), 378 ({N(Ar)C(H)}$_2$H$^+$, 43). IR ν/cm^{-1} (Nujol): 1661 m, 1610 m, 1260 m, 1098 m, 1020 m, 800 m. EI acc mass: on M$^+$: calc for $C_{47}H_{60}N_4AuGa$ 946.3734, found 946.3740.

Preparation of [(IPr)Cu{Ga{[N(Ar)C(H)]$_2$}}] (7). A solution of [K(tmeda)][:Ga{[N(Ar)C(H)]$_2$}] (0.22 g, 0.37 mmol) in THF (10 cm^3) was added to a suspension of [(IPr)CuCl] (0.18 g, 0.37 mmol) in THF (10 cm^3) at −78 °C to give a yellow solution. The reaction mixture was warmed to 20 °C and stirred overnight. Volatiles were removed *in vacuo*, and the residue was extracted into diethyl ether (50 cm^3) and filtered. The filtrate was concentrated to ca. 10 cm^3 and stored at −30 °C overnight to give yellow blocks of **7** (0.24 g, 73%). Mp: 160−164 °C (dec). ^{1}H NMR (400 MHz, C$_6$D$_6$, 298 K): δ 1.13 (d, $^3J_{HH}$ = 6.9 Hz, 12 H, (C*H*$_3$)$_2$CH), 1.16 (d, $^3J_{HH}$ = 6.9 Hz, 12 H, (C*H*$_3$)$_2$CH), 1.21 (d, $^3J_{HH}$ = 6.9 Hz, 12 H, (C*H*$_3$)$_2$CH), 1.50 (d, $^3J_{HH}$ = 6.9 Hz, 12 H, (C*H*$_3$)$_2$CH), 2.46 (sept, $^3J_{HH}$ = 6.9 Hz, 4 H, C*H*(CH$_3$)$_2$), 3.82 (sept, $^3J_{HH}$ = 6.9 Hz, 4 H, C*H*(CH$_3$)$_2$), 6.16 (s, 2 H, NC*H*), 6.58 (s, 2 H, NC*H*), 7.10−7.32 (m, 12 H, Ar-*H*). ^{13}C{^{1}H} NMR (75.6 MHz, C$_6$D$_6$, 298 K): δ 23.1, 24.4, 25.0, 26.3 (CH(*C*H$_3$)$_2$), 27.7, 28.6 (*C*H(CH$_3$)$_2$), 121.3, 123.8 (HCN), 121.9, 122.1, 123.9, 130.4, 134.1, 145.4, 145.9, 147.7 (Ar-*C*), 182.7 (br, *C*N$_2$). MS (EI 70 eV), *m/z* (%): 898 (MH$^+$, 36), 451 (Ga{N(Ar)C(H)}$_2$H$^+$, 50), 390 (IPrH$^+$, 100), 378 ({N(Ar)C(H)}$_2$H$^+$, 27). IR ν/cm^{-1} (Nujol): 1662 m, 1574 m, 1405 m, 1322 m, 1262 m, 1060 m, 934 m, 802 m. EI acc mass: on M$^+$: calc for $C_{53}H_{72}N_4CuGa$ 896.4303, found 896.4323. $C_{53}H_{72}N_4CuGa$ requires C 70.85, H 8.08, N 6.23; found C 70.46, H 8.20, N 6.16.

Preparation of [(IPr)Ag{Ga{[N(Ar)C(H)]$_2$}}] (8). A solution of [K(tmeda)][:Ga{[N(Ar)C(H)]$_2$}] (0.25 g, 0.41 mmol) in THF (10 cm^3) was added to a suspension of [(IPr)AgCl] (0.22 g, 0.41 mmol) in THF (10 cm^3) at −78 °C to give a yellow solution. The reaction mixture was warmed to 20 °C and stirred overnight. All volatiles were removed *in vacuo*, and the residue was extracted into hexane (60 cm^3) and filtered. The filtrate was concentrated to ca. 20 cm^3 and stored at −30 °C overnight to give yellow blocks of **8** (0.27 g, 69%). Mp: 83−86 °C (dec). ^{1}H NMR (400 MHz, C$_6$D$_6$, 298 K): δ 1.24 (d, $^3J_{HH}$ = 6.9 Hz, 12 H, (C*H*$_3$)$_2$CH), 1.28 (d, $^3J_{HH}$ = 6.9 Hz, 12 H, (C*H*$_3$)$_2$CH), 1.37 (d, $^3J_{HH}$ = 6.9 Hz, 12 H, (C*H*$_3$)$_2$CH), 1.58 (d, $^3J_{HH}$ = 6.9 Hz, 12 H, (C*H*$_3$)$_2$CH), 2.52 (sept, $^3J_{HH}$ = 6.9 Hz, 4 H, C*H*(CH$_3$)$_2$), 3.96 (sept, $^3J_{HH}$ = 6.9 Hz, 4 H, C*H*(CH$_3$)$_2$), 6.37 (s, 2 H, NC*H*), 6.70 (s, 2 H, NC*H*), 7.18−7.47 (m, 12 H, Ar-*H*). ^{13}C{^{1}H} NMR (75.6 MHz, C$_6$D$_6$, 298 K): δ 23.4, 24.4, 24.7, 26.4 (CH(*C*H$_3$)$_2$), 27.6, 28.5 (*C*H(CH$_3$)$_2$), 121.5, 123.8

Table 2. Summary of Crystallographic Data for Compounds 2−8

	2·(hexane)	**3**·(hexane)	**4**	**5**·(hexane)$_{0.5}$	**6**·(hexane)$_{0.25}$	**7**·(diethyl ether)	**8**
empirical formula	$C_{61}H_{86}GaN_4Rh$	$C_{61}H_{86}GaIrN_4$	$C_{47}H_{60}CuGaN_4$	$C_{50}H_{67}AgGaN_4$	$C_{48.5}H_{63.5}AuGaN_4$	$C_{57}H_{82}CuGaN_4O$	$C_{53}H_{72}AgGaN_4$
fw	1047.97	1137.26	814.25	901.67	969.22	972.53	942.74
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	tetragonal	orthorhombic	orthorhombic
space group	$P2_1/c$	$P2_1/c$	$C2_c$	$P2_1/n$	$I4_1a$	$P2_12_12_1$	$Pna2_1$
a (Å)	11.521(2)	12.472(3)	23.502(5)	14.104(3)	37.796(5)	12.249(2)	20.768(4)
b (Å)	20.938(4)	22.889(5)	13.040(3)	22.068(4)	37.796(5)	19.506(4)	11.945(2)
c (Å)	23.518(5)	20.442(4)	29.209(6)	16.348(3)	14.331(3)	23.836(5)	21.231(4)
β (deg)	91.01(3)	107.03(3)	90.26(3)	108.55(3)	90	90	90
vol (Å^3)	5673(2)	5579.7(19)	8952(3)	4824.2(17)	20473(6)	5695(2)	5266.9(18)
Z	4	4	8	4	16	4	4
ρ(calcd) (g·cm^{-3})	1.227	1.354	1.208	1.241	1.258	1.134	1.189
μ (mm^{-1})	0.806	2.906	1.111	1.000	3.421	0.885	0.918
F(000)	2224	2352	3440	1892	7880	2080	1984
cryst size (mm)	0.50 × 0.20 × 0.18	0.25 × 0.20 × 0.18	0.30 × 0.20 × 0.20	0.35 × 0.20 × 0.15	0.15 × 0.15 × 0.10	0.30 × 0.20 × 0.15	0.50 × 0.35 × 0.25
θ range (deg)	3.04 to 27.00	3.17 to 28.28	3.11 to 25.00	2.95 to 27.00	2.94 to 26.00	3.06 to 26.00	3.23 to 25.99
no. of reflns collected	24000	27195	12694	20118	55318	32725	48963
R_{int}	0.0277	0.0218	0.0342	0.0255	0.0746	0.0372	0.1128
no. of data/restraints/ params	12 362/5/590	13 811/0/620	7569/0/492	10 476/4/540	10 035/33/518	11 148/46/617	10 299/13/549
goodness of fit on F^2	1.022	1.032	1.065	1.025	1.067	1.029	1.019
R1 indices [$I > 2\sigma(I)$]^a	0.0392	0.0258	0.0426	0.0313	0.0382	0.0339	0.0469
wR2 indices (all data)^b	0.0984	0.0587	0.1053	0.0720	0.0986	0.0792	0.1244
largest peak and hole (e·A^{-3})	0.989 and −0.592	1.274 and −0.911	0.489 and −0.465	0.359 and −0.369	1.039 and −0.560	0.447 and −0.294	0.577 and −0.750

^{a} $R1(F) = \{\sum(|F_o| - |F_c|)/\sum|F_o|\}$ for reflections with $F_o > 4(\sigma(F_o))$. ^{b} $wR2(F^2) = \{\sum w(|F_o|^2 - |F_c|^2)^2/\sum w|F_o{}^2|^2\}^{1/2}$ where *w* is the weight given each reflection.

(H*C*N), 122.2, 123.5, 123.9, 130.4, 134.4, 145.4, 145.8, 147.3 (Ar-*C*), *C*N_2 not observed. MS (EI 70 eV), *m/z* (%): 941 (M^+, 3), 390 ($IPrH^+$, 73). IR ν/cm^{-1} (Nujol): 1662 m, 1590 m, 1551 m, 1407 m, 1356 m, 1257 m, 1113 m, 801 m. EI acc mass: on M^+: calc for $C_{53}H_{72}N_4AgGa$ 940.4058, found 940.4061. $C_{53}H_{72}N_4AgGa$ requires C 67.52, H 7.70, N 5.94; found C 67.32, H 7.68, N 5.90.

Preparation of [(IPr)Au{Ga{[N(Ar)C(H)]$_2$}}] (9). A solution of [K(tmeda)][:Ga{[N(Ar)C(H)]$_2$}] (0.22 g, 0.37 mmol) in THF (10 cm^3) was added to a suspension of [(IPr)AuCl] (0.23 g, 0.37 mmol) in THF (10 cm^3) at −78 °C to give a yellow solution. The reaction mixture was warmed to 20 °C and stirred overnight. Volatiles were removed *in vacuo*, and the residue was extracted into hexane (35 cm^3) and filtered. The filtrate was concentrated to ca. 10 cm^3 and stored at −30 °C to give yellow blocks of **9** (0.22 g, 58%). Mp: 80−83 °C (dec). ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ 0.98 (d, $^3J_{HH} = 6.9$ Hz, 12 H, (C*H*$_3$)$_2$CH), 1.09 (d, $^3J_{HH} = 6.9$ Hz, 12 H, (C*H*$_3$)$_2$CH), 1.12 (d, $^3J_{HH} = 6.9$ Hz, 12 H, (C*H*$_3$)$_2$CH), 1.33 (d, $^3J_{HH} = 6.9$ Hz, 12 H, (C*H*$_3$)$_2$CH), 2.32 (sept, $^3J_{HH} = 6.9$ Hz, 4 H, C*H*(CH$_3$)$_2$), 3.66 (sept, $^3J_{HH} = 6.9$ Hz, 4 H, C*H*(CH$_3$)$_2$), 6.09 (s, 2 H, NC*H*), 6.42 (s, 2 H, NC*H*), 6.95−7.18 (m, 12 H, Ar-*H*). ^{13}C{^{1}H} NMR (75.6 MHz, C_6D_6, 298 K): δ 23.4, 24.2, 24.5, 26.3 (CH(*C*H$_3$)$_2$), 27.7, 28.6 (*C*H(CH$_3$)$_2$), 120.8, 123.8 (H*C*N), 122.2, 123.8, 124.1, 130.4, 133.9, 145.4, 146.0, 146.7 (Ar-*C*), *C*N_2 not observed. MS (EI 70 eV), *m/z* (%): 1030 (M^+, 8), 390 ($IPrH^+$, 78). IR ν/cm^{-1} (Nujol): 1670 m, 1589 m, 1572 m, 1413 m, 1321 m, 1261 m, 865 m. EI acc. mass: on M^+: calc for $C_{53}H_{72}N_4AuGa$ 1030.4673, found 1030.4677. $C_{53}H_{72}N_4AuGa$ requires C 61.69, H 7.03, N 5.43; found C 61.37, H 7.05, N 5.49.

Preparation of [(ICy)Cu{Ga{[N(Ar)C(H)]$_2$}}] (10). A solution of [K(tmeda)][:Ga{[N(Ar)C(H)]$_2$}] (0.25 g, 0.41 mmol) in THF (10 cm^3) was added to a suspension of [(ICy)CuCl] (0.15 g, 0.41 mmol) in THF (10 cm^3) at −78 °C to give a yellow solution. The reaction mixture was warmed to 20 °C and stirred for 3 h. Volatiles were removed *in vacuo*, and the residue was extracted into hexane (40 cm^3) and filtered. The filtrate was concentrated to ca. 15 cm^3 and stored at −30 °C to give yellow blocks of **10** (0.13 g, 44%). Mp 155−160 °C (dec). ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ 1.11−2.36 (m, 20 H, C*H*$_2$), 1.48 (s, 6 H, Me), 1.56 (d, $^3J_{HH} = 6.9$ Hz, 12 H, (C*H*$_3$)$_2$CH), 1.62 (d, $^3J_{HH} = 6.9$ Hz, 12 H, (C*H*$_3$)$_2$CH), 3.39 (m, 2 H, C*H*CH$_2$), 4.08 (sept, $^3J_{HH} = 6.9$ Hz, 4 H, C*H*(CH$_3$)$_2$), 6.71 (s, 2 H, NC*H*), 7.36 (t, $^3J_{HH} = 7.2$ Hz, 2 H, *p*-Ar-*H*), 7.42 (d, $^3J_{HH} = 7.2$ Hz, 4 H, *m*-Ar-*H*). ^{13}C{^{1}H} NMR (75.6 MHz, C_6D_6, 298 K): δ 8.1 (Me), 24.6, 28.0 (CH(*C*H$_3$)$_2$), 26.2, 28.6, 36.7 (CH$_2$), 57.0 (N*C*H(CH$_2$)$_2$), 121.8, 124.1 (H*C*N), 122.2 (*m*-Ar*C*), 122.6 (*p*-Ar*C*), 146.0 (*o*-Ar*C*), 148.3 (*ipso*-Ar*C*), 173.7 (br, *C*N_2). MS (EI 70 eV), *m/z* (%): 768 (MH^+, 65), 445 (Ga{N(Ar)C(H)}$_2$H$^+$, 24), 378 ({N(Ar)C(H)}$_2$H$^+$, 100). IR ν/cm^{-1} (Nujol): 1643 m, 1585 m, 1548 m, 1260 m, 1098 m, 1057 m. EI acc mass: on M^+: calc for $C_{43}H_{64}N_4CuGa$ 768.3677, found 768.3682. $C_{43}H_{64}N_4CuGa$ requires C 67.05, H 8.37, N 7.27; found C 67.21, H 8.65, N 7.48.

X-ray Crystallography. Crystals of **2**−**8** suitable for X-ray structural determination were mounted in silicone oil. Crystallographic measurements were made using a Nonius Kappa CCD diffractometer using a graphite monochromator with Mo Kα radiation ($\lambda = 0.71073$ Å). The data were collected at 150 K, and the structures were solved by direct methods and refined on F^2 by full matrix least-squares (SHELX97)[40] using all unique data. All non-hydrogen atoms are anisotropic with hydrogen atoms included in calculated positions (riding model). The Flack parameter for the structure of **7** is 0.002(8). The Flack parameter for the structure of **8** converged to 0.238(14) after refinement as a racemic twin. Crystal data, details of data collections, and refinement are given in Table 2.

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Supporting Information Available: Crystallographic data as CIF files for **2**−**8** and [Au(IPr)$_2$][Ga{[N(Ar)C(H)]$_2$}$_2$]; ORTEP diagrams for **3**, **5**−**7**, and [Au(IPr)$_2$][Ga{[N(Ar)C(H)]$_2$}$_2$]; selected metrical parameters for [Au(IPr)$_2$][Ga{[N(Ar)C(H)]$_2$}$_2$]; and the ^{1}H NMR spectrum of **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(40) Sheldrick, G. M. *SHELX-97*; University of Göttingen, 1997.