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Synthesis and characterisation of zinc gallyl complexes: First structural elucidations of Zn–Ga bonds†‡

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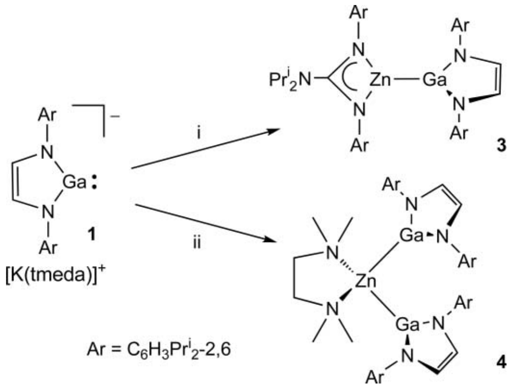
Reactions of the anionic gallium(I) heterocycle, [:Ga{[N(Ar)-C(H)]$_2$}]$^-$ (Ar = C$_6$H$_3$Pr$^i_2$-2,6), with two N,N-chelated zinc chloride complexes have yielded the compounds, [{Pr$^i_2$NC[N(Ar)]$_2$}ZnGa{[N(Ar)C(H)]$_2$}] and [(tmeda)Zn-{Ga{[N(Ar)C(H)]$_2$}}$_2$] which contain the first crystallographically characterised Zn–Ga bonds.

The chemistry of complexes containing metal–metal bonds is wide ranging and of undoubted fundamental importance. Over the years such complexes have found numerous applications in synthesis, catalysis and materials chemistry to name but a few.[1] We gained entry to this field with the synthesis of the anionic gallium(I) heterocycle, [:Ga{[N(Ar)C(H)]$_2$}]$^-$ **1** (Ar = C$_6$H$_3$Pr$^i_2$-2,6),[2] which is a valence isoelectronic analogue of the important N-heterocyclic carbene (NHC) class of ligand. This has been utilised in a variety of ligand displacement, oxidative insertion and reductive elimination reactions that have yielded an array of complexes containing bonds between gallium and s-, p- or d-block metals. In addition, the carbenoid character of **1** has proved useful in cycloaddition and C–H activation reactions.[3,4]

Until recently, the formation of metal gallyl complexes from the reactions of **1** with metal halides and their complexes had proved elusive. Instead of salt elimination occurring, the paramagnetic gallium(II) dimers, [GaX{[N(Ar)C(H)$^\bullet$]$_2$}]$_2$ (X = halide), were invariably formed in these reactions.[5] These presumably resulted from 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 dimer. We now know that the problems associated with reactions of **1** with metal halides can be circumvented by pre-coordination of the metal halide reactant with bulky and/or electron rich ligands, *e.g.* NHCs or bulky guanidinates. As a result, neutral metal gallyl complexes are becoming increasing accessible, which in the last 12 months have included examples containing the first structurally characterised Ga–Sn,[4a] Ga–Nd,[6] Ga–Cu[7] and Ga–Ag[7] bonds. An extension of this work to the preparation of zinc gallyl complexes seemed appropriate as Zn–Ga bonded species were unknown prior to this study, despite the relatively well developed chemistry of zinc–metal bonded compounds.[1,8] It was also seen of interest as gallium is adjacent to zinc in the periodic table, and therefore the properties of the two metals are not dissimilar. Given that the molecular chemistry of zinc(I) has been initiated with the preparation of remarkable compounds of the general type, RZn^{I}Zn^{I}R,[9] comparisons with related Zn–Ga bonded complexes would be informative. Our preliminary efforts to form zinc gallyl complexes are reported herein.

The bulky guanidinate ligand, [Pr$^i_2$NC{N(Ar)}$_2$]$^-$ (Priso$^-$), has been shown to be effective in the stabilisation of the first structurally characterised Sn–Ga bonded complex [(Priso)SnGa{[N(Ar)C(H)]$_2$}].[4a] Accordingly, it was employed in this study to form the zinc chloride complex, [(Priso)ZnCl] **2**,‡ which when reacted with [K(tmeda)][**1**] in toluene afforded the zinc gallyl, **3**, in almost quantitative yield (Scheme 1). In order to examine the possibility of preparing a bis(gallyl) zinc complex, [ZnCl$_2$(tmeda)] was treated with two equivalents of [K(tmeda)][**1**] which afforded **4** in good yield. Repeating this reaction in a 1 : 1 stoichiometry led to no isolable products. Similarly, the 2 : 1 reaction of [K(tmeda)][**1**] with [CdCl$_2$(tmeda)] led to decomposition and deposition of cadmium metal above 0 °C, thus attesting to the reducing nature of **1**.



Scheme 1 *Reagents and conditions*: (i), (Priso)ZnCl **2**, –KCl; (ii), 1/2 (tmeda)ZnCl$_2$, –KCl.

Both **3** and **4** are yellow crystalline solids that are indefinitely stable under inert atmospheres. The NMR spectra of **3** § are consistent with its proposed structure in that they exhibit resonances corresponding to five chemically inequivalent sets of isopropyl methyl groups. In contrast, the ^{1}H NMR spectrum of **4** displays only two broadened isopropyl methyl doublet resonances, which suggests rotation of its gallyl groups about the Zn–Ga bonds in solution. Variable temperature NMR studies (298 K–223 K) led to further broadening of these signals, but not to resolution of the spectrum.

Compounds **3** and **4** were crystallographically characterised†¶ and their molecular structures are depicted in Fig. 1 and 2 respectively. It should be noted that the quality of the structure of

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† CCDC reference numbers 645310 and 645311. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b706402k

‡ Electronic supplementary information (ESI) available: Full synthetic details for **2–4**. See DOI: 10.1039/b706402k

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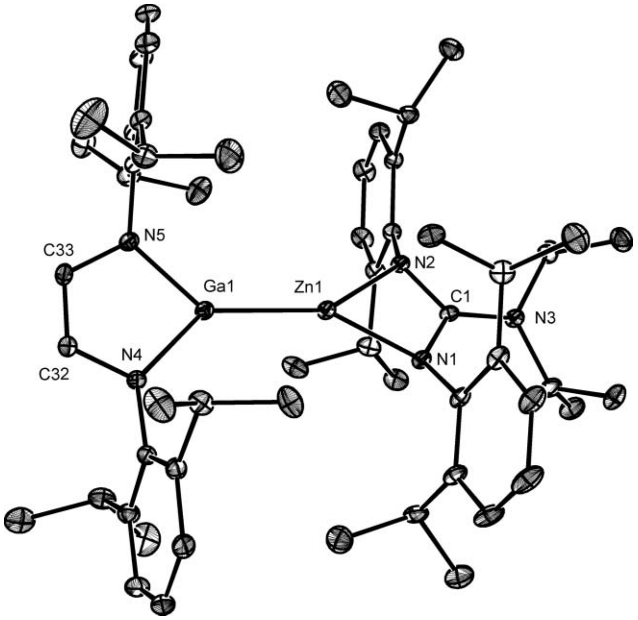

Fig. 1 Molecular structure of **3** (25% thermal ellipsoids, hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): Ga(1)–N(4) 1.8633(19), Ga(1)–N(5) 1.867(2), Ga(1)–Zn(1) 2.3230(7), Zn(1)–N(1) 1.986(2), Zn(1)–N(2) 2.0041(19), N(1)–C(1) 1.354(3), N(2)–C(1) 1.356(3), N(3)–C(1) 1.360(3), N(4)–C(32) 1.383(3), N(5)–C(33) 1.392(3), C(32)–C(33) 1.338(4), N(4)–Ga(1)–N(5) 88.12(9), N(1)–Zn(1)–N(2) 67.40(8), N(1)–C(1)–N(2) 109.5(2).

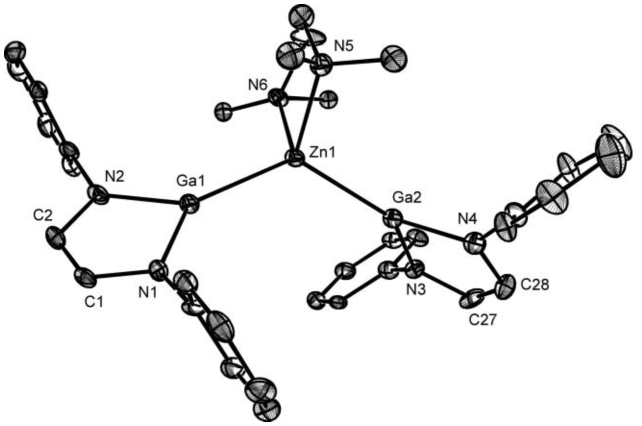

Fig. 2 Molecular structure of **4** (25% thermal ellipsoids, hydrogen atoms and isopropyl groups omitted). Selected bond lengths (Å) and angles (°): Ga(1)–N(2) 1.905(10), Ga(1)–N(1) 1.903(9), Ga(1)–Zn(1) 2.4491(17), Ga(2)–N(4) 1.886(10), Ga(2)–N(3) 1.895(8), Ga(2)–Zn(1) 2.4307(17), Zn(1)–N(6) 2.168(9), Zn(1)–N(5) 2.177(10), N(2)–Ga(1)–N(1) 86.2(4), N(4)–Ga(2)–N(3) 86.7(4), N(6)–Zn(1)–N(5) 84.7(3), Ga(2)–Zn(1)–Ga(1) 126.00(6).

4 is poor due to significant disorder of its tmeda ligand and the weakly diffracting nature of its crystals. Despite this, the molecular connectivity of the complex is unambiguous and the geometrical parameters of its $ZnGa_2N_2$ fragment are sufficiently accurate to pass comment. Both compounds are monomeric with distorted trigonal planar (**3**) or tetrahedral (**4**) zinc coordination geometries. The geometries of the gallium heterocycles in **3** and **4** are similar to each other and to those in the majority of other complexes of **1**.[3,4] As in previously reported zinc guanidinate complexes,[10] the backbone N–C distances in the guanidinate ligand of **3** are suggestive of significant delocalisation over its N_3C fragment. Although there have been no previously reported Zn–Ga bonds for purposes of comparison, the bond lengths characterised in this study are well within the sum of covalent radii (2.50 Å[11]) for the two elements. Interestingly however, that in **3** it is *ca.* 0.1 Å shorter than those in **4**, probably because of the differences in the zinc coordination numbers between the two complexes. As the covalent radii of zinc and gallium are the same (1.25 Å[11]), the Zn–Ga bonds in **3** and **4** are, not surprisingly, of similar lengths to the four previously structurally characterised Zn^I–Zn^I interactions (range: 2.305(3) Å–2.3994(6) Å[9]).

One feature of the structure of **3** that interested us was the acute angle between the least squares planes of its two heterocycles (21.7°). As the two metal centres of the compound presumably possess empty p-orbitals orthogonal to the heterocycle planes, the possibility of singly or doubly reducing **3** to give a complex with a Zn–Ga bond order of 1.5 or 2 respectively, existed. In this respect, similar single reductions of digallanes, $[R_2GaGaR_2]$, have previously afforded planar radical anions, $[R_2GaGaR_2]^{\bullet-}$, with a Ga–Ga bond order of 1.5.[12] Attempts to cleanly reduce **3** with lithium or KC_8 in 1 : 1 or 2 : 1 stoichiometries have so far not been successful and instead have led to an intractable mixtures of products.

In conclusion, the first examples of complexes containing Zn–Ga bonds have been described. We are currently exploring the reactivity of the metal–metal bonds in the prepared complexes towards Lewis bases and mild reducing agents and will report on this in due course.

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Notes and references

§ *Selected data for* **3**: Yield: 96% (yellow crystals). Mp 180–185 °C (dec.). ^1H NMR (400 MHz, C_6D_6, 298 K): δ 0.81 (d, $^3J_{HH}$ = 6.8 Hz, 12 H, $NCH(CH_3)_2$), 1.13 (d, $^3J_{HH}$ = 6.8 Hz, 12 H, $CH(CH_3)_2$), 1.16 (d, $^3J_{HH}$ = 6.8 Hz, 12 H, $CH(CH_3)_2$), 1.39 (d, $^3J_{HH}$ = 6.8 Hz, 12 H, $CH(CH_3)_2$), 1.51 (d, $^3J_{HH}$ = 6.8 Hz, 12 H, $CH(CH_3)_2$), 3.60 (overlapping m, 6 H, $CH(CH_3)_2$), 3.79 (sept, $^3J_{HH}$ = 6.8 Hz, 4 H, $CH(CH_3)_2$), 6.36 (s, 2 H, GaNC*H*), 7.03–7.39 (m, 12 H, Ar*H*); $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6, 298 K): δ 20.5, 20.7, 22.2, 23.0, 24.2 ($CH(CH_3)_2$), 27.0, 27.8 ($CH(CH_3)_2$), 47.8 ($NCH(CH_3)_2$), 121.4 (N=C), 121.5, 121.7, 121.9, 123.4, 141.6, 143.9, 144.2, 146.4 (Ar*C*), 168.4 (CN_3); IR ν/cm^{-1} (Nujol): 1613 (s), 1584 (m), 1260 (m), 1124 (m), 1107 (m), 1057 (m), 932 (m), 800 (m); MS (EI 70 eV), *m/z* (%): 971 (M^+, 2), 420 [$(ArN)_2CNPr^iH^+$, 100]; EI Acc. Mass.: calc. for $C_{57}H_{84}N_5{}^{69}GaZn$: 971.5269, found: 971.5268; **4**: Yield: 72% (yellow crystals). Mp 85–87 °C. ^1H NMR (400 MHz, C_6D_6, 298 K): δ 1.18 (br. d, $^3J_{HH}$ = 6.8 Hz, 24H, $CH(CH_3)_2$), 1.33 (br. d, $^3J_{HH}$ = 6.8 Hz, 24H, $CH(CH_3)_2$), 1.42 (s, NCH_2, 4H), 1.47 (s, NCH_3, 12H), 3.64 (sept, $^3J_{HH}$ = 6.8 Hz, 8 H, $CH(CH_3)_2$), 6.37 (s, NCH, 4H), 7.13–7.18 (m, ArH, 12H); ^{13}C NMR (75 MHz, C_6D_6, 298 K): δ 23.5, 24.4 (br., $CH(CH_3)_2$), 26.7 (br., $CH(CH_3)_2$), 47.7 (NCH_3), 55.8 (NCH_2), 121.5 (CN), 121.7 (*m*-ArC), 123.3 (*p*-ArC), 144.1 (*o*-ArC), 146.3 (*ipso*-ArC); IR ν/cm^{-1} (Nujol): 1587 (s), 1259 (s), 1100 (br), 1020 (br), 800 (s); MS (EI 70 eV), *m/z* (%): 1071 (M^+, 2), 446 ($Ga\{[N(Ar)C(H)]_2\}^+$, 12), 377 ($\{N(Ar)C(H)\}_2H^+$, 100); EI Acc. Mass.: calc. for $C_{58}H_{88}N_6{}^{69}Ga_2Zn$: 1070.4873, found: 1070.4870.

¶ *Crystal data* for **3**: $C_{57}H_{84}GaN_5Zn$, M = 974.38, triclinic, space group *P*-1, a = 11.608(2) Å, b = 13.803(3) Å, c = 17.997(4) Å, α = 88.49(3)°,

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$\beta = 81.17(3)°$, $\gamma = 86.69(3)°$, $V = 2844.3(10)$ Å^3, $Z = 2$, $D_c = 1.138$ g cm^{-3}, $F(000) = 1044$, μ(Mo-Kα) = 0.933 mm^{-1}, 150(2) K, 10 462 unique reflections [$R_{(int)}$ 0.0349], R (on F) 0.0418, wR (on F^2) 0.0950 ($I > 2\sigma I$); **4**·(diethyl ether)$_{0.5}$: $C_{60}H_{93}Ga_2N_6O_{0.5}Zn$, M = 1111.21, orthorhombic, space group *Pbca*, a = 13.953(3) Å, b = 21.070(4) Å, c = 46.243(9) Å, V = 13595(5) Å^3, $Z = 8$, $D_c = 1.086$ g cm^{-3}, $F(000) = 4728$, μ(Mo-Kα) = 1.173 mm^{-1}, 150(2) K, 11 852 unique reflections [$R_{(int)}$ 0.0854], R (on F) 0.1271, wR (on F^2) 0.3003 ($I > 2\sigma I$).

1 (*a*) e.g.F. A. Cotton and R. A. Walton, *Multiple Bonds between Metal Atoms*, 2nd edn, Oxford University Press, New York, 1993; (*b*) L. H. Gade, *Angew. Chem., Int. Ed.*, 2000, **39**, 2658; (*c*) F. A. Cotton, *Inorg. Chem.*, 1998, **37**, 5710, and references therein.

2 R. J. Baker, R. D. Farley, C. Jones, M. Kloth and D. M. Murphy, *J. Chem. Soc., Dalton Trans.*, 2002, 3844 A synthesis of a related anion, [:Ga{[N(Bu^t)C(H)]$_2$}]$^-$, has been previously reported, see: E. S. Schmidt, A. Jockisch and H. Schmidbaur, *J. Am. Chem. Soc.*, 1999, **121**, 9358.

3 R. J. Baker and C. Jones, *Coord. Chem. Rev.*, 2005, **149**, 1857, and references therein.

4 (*a*) S. P. Green, C. Jones, K.-A. Lippert, D. P. Mills and A. Stasch, *Inorg. Chem.*, 2006, **45**, 7242; (*b*) S. Aldridge, R. J. Baker, N. D. Coombs, C. Jones, R. P. Rose, A. Rossin and D. J. Willock, *Dalton Trans.*, 2006, 3313; (*c*) R. J. Baker, C. Jones, D. P. Mills, D. M. Murphy, E. Hey-Hawkins and R. Wolf, *Dalton Trans.*, 2006, 64; (*d*) C. Jones, D. P. Mills and R. P. Rose, *J. Organomet. Chem.*, 2006, **691**, 3060; (*e*) R. J. Baker, C. Jones and D. M. Murphy, *Chem. Commun.*, 2005, 1339; (*f*) R. J. Baker, C. Jones and M. Kloth, *Dalton Trans.*, 2005, 2106; (*g*) R. J. Baker, C. Jones, M. Kloth and J. A. Platts, *Organometallics*, 2004, **23**, 4811; (*h*) R. J. Baker, C. Jones, M. Kloth and J. A. Platts, *Angew. Chem., Int. Ed.*, 2003, **43**, 2660; (*i*) R. J. Baker, C. Jones and J. A. Platts, *Dalton Trans.*, 2003, 3673; (*j*) R. J. Baker, C. Jones and J. A. Platts, *J. Am. Chem. Soc.*, 2003, **125**, 10534.

5 R. J. Baker, R. D. Farley, C. Jones, M. Kloth, D. P. Mills and D. M. Murphy, *Chem.–Eur. J.*, 2005, **11**, 2972.

6 P. L. Arnold, S. T. Liddle, J. McMaster, C. Jones and D. P. Mills, *J. Am. Chem. Soc.*, 2007, **129**, 5360.

7 S. P. Green, C. Jones, D. P. Mills and A. Stasch, *Organometallics*, DOI: 10.1021/om700345m.

8 As determined from a survey of the Cambridge Crystallographic Database, April, 2007.

9 (*a*) I. Resa, E. Carmona, E. Gutierrez-Puebla and A. Monge, *Science*, 2004, **305**, 1136; (*b*) Y. Wang, B. Quillian, P. Wei, H. Wang, X.-J. Yang, Y. Xie, R. B. King, P. v. R. Schleyer, H. F. Schaefer, III and G. H. Robinson, *J. Am. Chem. Soc.*, 2005, **127**, 11944; (*c*) Z. Zhu, R. J. Wright, M. M. Olmstead, E. Rivard, M. Brynda and P. P. Power, *Angew. Chem., Int. Ed.*, 2006, **45**, 5807; (*d*) X. J. Yang, J. Yu, Y. Liu, Y. Xie, H. F. Schaefer, Y. Liang and B. Wu, *Chem.Commun.*, 2007, 2363.

10 M. P. Coles and P. B. Hitchcock, *Eur. J. Inorg. Chem.*, 2004, 2662.

11 J. Emsley, *The Elements*, 2nd edn, Clarendon Press, Oxford, UK, 1991.

12 (*a*) W. Uhl, U. Schütz, W. Kaim and E. Waldhör, *J. Organomet. Chem.*, 1995, **501**, 79; (*b*) X. He, R. A. Bartlett, M. M. Olmstead, K. R. Senge, B. A. Sturgeon and P. P. Power, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 717.