

# Evidence for the first oxidative insertion of a transition metal into a digallane(4): synthesis, structural characterisation and EPR studies of $[\text{Cp}_2\text{Zr}^{\text{III}}\{\text{Ga}[\text{N}(\text{Ar})\text{C}(\text{H})]_2\}_2][\text{Li}(\text{THF})_4]$ , $\text{Ar} = \text{C}_6\text{H}_3\text{Pr}^i_{2-2,6}$

Robert J. Baker, Cameron Jones\* and Damien M. Murphy

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Treatment of “ $\text{ZrCp}_2$ ” with the digallane(4),  $[\{\text{Ga}[\text{N}(\text{Ar})\text{C}(\text{H})]_2\}_2]$ ,  $\text{Ar} = \text{C}_6\text{H}_3\text{Pr}^i_{2-2,6}$ , in the presence of excess  $\text{Bu}^n\text{Li}$  leads to the first example of a gallyl–Group 4 complex,  $[\text{Cp}_2\text{Zr}\{\text{Ga}[\text{N}(\text{Ar})\text{C}(\text{H})]_2\}_2][\text{Li}(\text{THF})_4]$ , via an unprecedented oxidative insertion reaction; the paramagnetic complex has been characterised by X-ray crystallography and EPR spectroscopy.

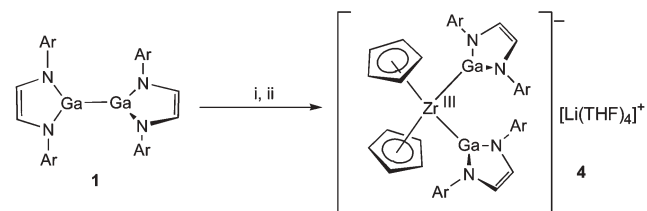
The oxidative insertion of transition metal fragments into the B–B bond of diboranes(4), e.g. bis(catecholato)- or bis(pinacolato)-diborane, has been widely studied.<sup>1</sup> A number of the resulting bis(boryl)–transition metal complexes have been implicated as intermediates in important synthetic processes such as the catalytic diborylation of unsaturated substrates.<sup>2</sup> Similarly, the field of digallane(4) chemistry is now well established and the further chemistry of such compounds has been extensively investigated.<sup>3</sup> However, to the best of our knowledge, there have been no reports of the oxidative insertion of transition metal fragments into the Ga–Ga bond of digallanes(4), though a small number of related metathesis reactions between  $[\text{Ga}_2\text{Cl}_4(\text{L})_2]$  ( $\text{L} = \text{dioxane}$  or  $\text{THF}$ ) and M–M bonded species have been described (e.g. as in the synthesis of  $[\text{CpFe}(\text{CO})_2\{\text{GaCl}_2(\text{THF})\}]$ ).<sup>4</sup> In addition, the oxidative insertion of, for example, organic acids and chalcogens into digallanes(4) have been reported by Uhl *et al.*<sup>3</sup>

We have recently shown that the digallane(4),  $[\{\text{Ga}[\text{N}(\text{Ar})\text{C}(\text{H})]_2\}_2]$  **1**,  $\text{Ar} = \text{C}_6\text{H}_3\text{Pr}^i_{2-2,6}$ , can be prepared in high yield via oxidative coupling<sup>5</sup> of the anionic gallium(I) heterocycle,  $[\text{Ga}\{\text{N}(\text{Ar})\text{C}(\text{H})\}_2]^-$  **2**, which is a valence isoelectronic analogue of the important N-heterocyclic carbene (NHC) class of ligand.<sup>6</sup> It is worth noting here that **1** and a related digallane,  $[\{\text{Ga}[\text{N}(\text{Bu})\text{C}(\text{H})]_2\}_2]$ , have been previously prepared by alternative routes.<sup>7</sup> In light of Uhl’s work with digallanes and our recent success in utilising **2** as a ligand towards transition (and main group) metal fragments,<sup>8</sup> it seemed reasonable that (bis)gallyl–transition metal complexes might be prepared via oxidative insertion reactions involving **1**. Our preliminary efforts in this direction are reported herein.

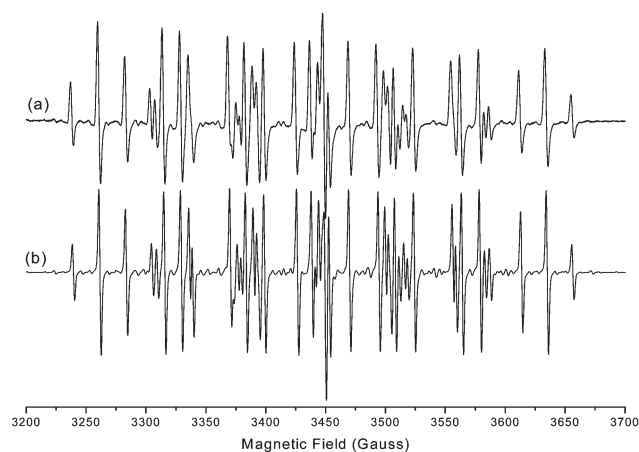
An attempt to form the gallyl– $\text{Zr}^{\text{IV}}$  complex,  $[\text{Cp}_2\text{Zr}\{\text{Ga}[\text{N}(\text{Ar})\text{C}(\text{H})]_2\}_2]$  **3**, via insertion of “ $\text{ZrCp}_2$ ” (generated *in situ* from  $\text{Cp}_2\text{ZrCl}_2$  and 2 equivs. of  $\text{Bu}^n\text{Li}$ ) into the Ga–Ga bond of **1** led, unexpectedly, to the closely related green  $\text{Zr}^{\text{III}}$  complex,  $[\text{Cp}_2\text{Zr}\{\text{Ga}[\text{N}(\text{Ar})\text{C}(\text{H})]_2\}_2][\text{Li}(\text{THF})_4]$  **4**, in low yield (ca. 10%) after warming the reaction mixture from  $-78$  °C to  $25$  °C. It is believed this resulted from the reduction of the intended product, **3**, by an unintentional excess of  $\text{Bu}^n\text{Li}$  in the reaction mixture (probably present as  $[\text{Cp}_2\text{ZrBu}^n_3][\text{Li}]^9$ ), though the exact

mechanism of this reduction is as yet unknown. Interestingly, **3** could not be isolated from (i) a repeat reaction employing the correct stoichiometry, (ii) the reaction of  $\text{Cp}_2\text{ZrCl}_2$  with 2 equivs. of the anion, **2**, or (iii) the chemical oxidation of **4** with  $\text{Ag}[\text{BF}_4]$  or  $[\text{Cp}_2\text{Fe}][\text{PF}_6]$ . In all cases intractable product mixtures resulted. This raises the possibility that **3** is only transiently stable in solution at room temperature, which would be surprising considering the thermal stability of **4** (decomp.  $277$ – $281$  °C). Moreover, the formation of **4** is unusual in itself given the fact that the reduction of  $\text{Zr}^{\text{IV}}$  to  $\text{Zr}^{\text{III}}$  species by alkyl lithium reagents is extremely rare.<sup>10</sup> Indeed, if our proposal for the formation of **4** is correct it would imply that **3** is much more readily reduced than is general for cyclopentadienyl zirconium(IV) complexes,<sup>11</sup> though attempts to quantify the oxidation potential of **4** (and thus the reduction potential of **3**) by electrochemical means have so far met with failure. With respect to the stability of **3**, it is worth noting a very recent precedent for the stabilisation of low oxidation state zirconocene complexes by incorporation of low valent gallium donor ligands; specifically in the formally  $\text{Zr}^{\text{II}}$  complex  $[\text{Cp}_2\text{Zr}(\text{GaAr}')_2]$  **5**,  $\text{Ar}' = \text{C}_6\text{H}_3(\text{C}_6\text{H}_2\text{Pr}^i_{3-2,4,6})_{2-2,6}$ .<sup>12</sup>

A higher yield (64%) route† to **4** was devised whereby *in situ* generated “ $\text{ZrCp}_2$ ” was treated with 1 equiv. of **1** at  $-50$  °C, after which the mixture was warmed to  $-10$  °C before treatment with 1 equiv. of  $\text{Bu}^n\text{Li}$  (Scheme 1). The paramagnetic nature of **4** discounted useful NMR data being obtained for this complex. Its EPR spectrum was recorded at  $25$  °C and satisfactorily simulated using the spin Hamiltonian parameters of  $g_{\text{iso}} = 1.9735$ ,  $a_{\text{iso}} = 54.5$  G for  $^{69}\text{Ga}$  (60.1% abundance;  $I = 3/2$ ) and  $70.0$  G for  $^{71}\text{Ga}$  (39.9% abundance;  $I = 3/2$ ), assuming two equivalent gallium nuclei (Fig. 1). Owing to the excellent resolution of the spectrum, the low intensity lines arising from  $^{91}\text{Zr}$  (11.2% abundance;  $I = 5/2$ ) hyperfine coupling ( $a_{\text{iso}} = 15$  G) were also detected and accurately reproduced in the simulation. The  $g$ -value and  $^{91}\text{Zr}$  hyperfine coupling are in the normal range for dialkyl and dihalozirconoceneate(III) complexes.<sup>11</sup> Although the hyperfine couplings to  $^{69,71}\text{Ga}$  dominate the EPR spectrum, they still



**Scheme 1** Reagents and conditions: i, “ $\text{ZrCp}_2$ ”,  $\text{THF}$ ,  $-50$  °C; ii,  $\text{Bu}^n\text{Li}$ ,  $-10$  °C.

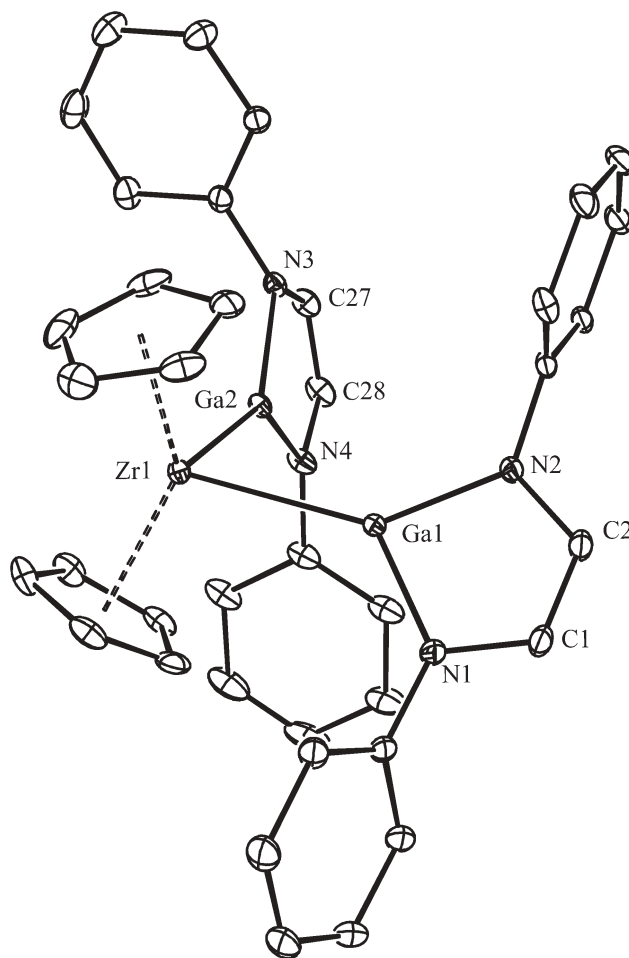


**Fig. 1** X-Band EPR spectrum of **4** recorded at room temperature. (a) experimental, (b) simulation.

represent a very small unpaired spin density on the two gallium nuclei (1.25%). This suggests that there is negligible back-bonding from the  $d^1$ -Zr centre into the empty p-orbitals of the gallily ligands. Couplings to the cyclopentadienyl protons and to the proton and nitrogen centres of the gallily ligands were not resolved in the EPR spectrum.

The structure of the anionic component of **4** is depicted in Fig. 2 and represents the first structural characterisation of a gallily-Group 4 complex and a rare example of a structurally authenticated zirconocenate(III) anion.<sup>‡</sup> It is worthy of note that there have been no reports of corresponding boryl-Group 4 complexes. The gallium centres in **4** have planar geometries ( $\Sigma$ angles about Ga 359.4° avge.) and the Zr–Ga distances [2.738 Å avge.] are significantly longer than in the only other complex to possess such bonds, *viz.* **5** [2.6350(8) Å].<sup>12</sup> This difference likely arises from the fact that in **5** the gallium centres are two-coordinate. Considering the bulk of the gallily ligands in **4** it is perhaps surprising that the Ga–Zr–Ga angle is appreciably more acute [87.70(3)°] than that of **5** [100.39(4)°], whilst the Cp centroid–Zr–Cp centroid angles are similar [**4**: 136.1°; **5**: 137.4°]. Furthermore, it is of interest to examine the geometry of the gallium heterocycles in **4**. As with the NCN fragment of N-heterocyclic carbenes,<sup>13</sup> we have shown that upon coordination to both transition and main group metals (as in for *e.g.* [CpNi{Ga[N(Ar)C(H)]<sub>2</sub>}]<sup>−8b</sup>), the NGaN fragment of the gallily ligand becomes more open (*ca.* 87°) and the N–Ga bonds shorter (*ca.* 1.90 Å) than in the free anionic heterocycle, **2** (*ca.* 82° and 2.0 Å respectively).<sup>6</sup> This arises from a loss of electron density from the nucleophilic gallium centre of the heterocycle to the coordinated metal centre. In complex **4** the magnitudes of the NGaN angles (85.0° avge.) and the N–Ga bond lengths (1.931 Å avge.) imply a weaker coordination of the gallium heterocycles than has previously been seen. This is additionally evidenced by the apparently long Zr–Ga bonds in the complex and is probably due to the considerable steric crowding about the zirconium centre. There are no structurally characterised examples of NHC–Zr(III) complexes to draw comparisons with here, but in the few NHC–Zr(IV) complexes that have been reported the NHC ligands seemingly act as a strong  $\sigma$ -donors.<sup>14</sup>

In conclusion, we have demonstrated the oxidative insertion of a transition metal centre into a digallane(4) for the first time. This



**Fig. 2** Structure of the anionic component of **4** (isopropyl groups and hydrogens omitted for sake of clarity). Selected bond lengths (Å) and angles (°): Zr(1)–Ga(1) 2.7417(7), Zr(1)–Ga(2) 2.7349(8), Ga(1)–N(1) 1.935(3), Ga(1)–N(2) 1.921(3), Ga(2)–N(3) 1.937(3), Ga(2)–N(4) 1.931(3), Zr(1)–Cp cent. 2.194 avge.; Ga(1)–Zr(1)–Ga(2) 87.70(3), Cp cent.–Zr(1)–Cp cent. 136.14(15), N(1)–Ga(1)–N(2) 84.87(14), N(3)–Ga(2)–N(4) 85.08(14), N(1)–Ga(1)–Zr(1) 131.99(10), N(2)–Ga(1)–Zr(1) 142.64(10), N(3)–Ga(2)–Zr(1) 136.99(10), N(4)–Ga(2)–Zr(1) 137.13(10).

has generated an unprecedented gallily–zirconium(III) complex which has been studied by X-ray crystallography and EPR spectroscopy. In light of the importance of oxidative insertions involving diboranes(4), we have embarked on a major study of the reactivity of **1** and related digallanes(4) toward low-valent early and late transition metal complexes. The preliminary indications of this study are that gallily ligands will be useful in stabilising unusual complexes, some of which have no counterparts in boryl coordination chemistry, *e.g.* [Cp<sub>2</sub>M<sup>III</sup>{Ga[N(Ar)C(H)]<sub>2</sub>}], M = Cr or V.<sup>15</sup> The full details of this study will be reported on in a forthcoming publication.

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**Robert J. Baker, Cameron Jones\* and Damien M. Murphy**  
Centre for Fundamental and Applied Main Group Chemistry, School of Chemistry, Cardiff University, Cardiff, P.O. Box 912, Park Place, Cardiff, UK CF10 3TB

## Notes and references

† *Synthesis and selected data for 4*: Compound **1** (0.15 g, 0.17 mmol) was added to a solution of “Cp<sub>2</sub>Zr” in THF (20 cm<sup>3</sup>) at –50 °C (prepared *in situ* from 0.17 mmol of Cp<sub>2</sub>ZrCl<sub>2</sub> and 0.34 mmol of <sup>n</sup>BuLi in hexanes). The resultant red solution was warmed to –10 °C and stirred for 1 hour, whereupon it was cooled to –50 °C and Bu<sup>n</sup>Li (0.17 mmol in hexanes) added. The solution was warmed to 25 °C, stirred overnight, and volatiles removed *in vacuo* to give a green solid after washing with hexane. This was recrystallised from THF/toluene (95 : 5, 10 cm<sup>3</sup>) at –35 °C. Yield (0.16 g, 64%). Mp 277–281 °C (decomp.); MS (–ve ion CI): *m/z* (%) 1114.0 [Cp<sub>2</sub>Zr{Ga[N(Ar)C(H)]<sub>2</sub>}<sub>2</sub><sup>–</sup>, 2%, accurate isotopic distribution], 446.3 [Ga{N(Ar)C(H)}<sub>2</sub><sup>–</sup>, 91%], 376.4 [{N(Ar)C(H)}<sub>2</sub><sup>–</sup>, 100%]; IR (Nujol)  $\nu$ /cm<sup>–1</sup> 1586 (m), 1556 (w), 1458 (s), 1433 (s), 1377 (m), 1354 (s), 1320 (m), 1255 (s), 1210 (m), 1191 (m), 1110 (m), 1041 (s), 1008 (w), 889 (m), 800 (m); UV/VIS (10<sup>–3</sup> M in THF) 226 nm ( $\epsilon > 15000$  dm<sup>3</sup> mol<sup>–1</sup> cm<sup>–1</sup>, CT), 266 nm ( $\epsilon = 11304$ , CT), d–d transitions not distinguishable.

‡ *Crystal data for 4* (toluene): C<sub>85</sub>H<sub>121</sub>Ga<sub>2</sub>LiN<sub>4</sub>O<sub>4</sub>Zr, *M* = 1500.46 monoclinic, space group *P*2<sub>1</sub>/*c*, *a* = 15.171(3), *b* = 21.373(4), *c* = 26.866(5) Å,  $\beta$  = 105.13(3)°, *V* = 8409(3) Å<sup>3</sup>, *Z* = 4, *D*<sub>c</sub> = 1.185 g cm<sup>–3</sup>, *F*(000) = 3184,  $\mu$ (Mo–K $\alpha$ ) = 0.805 mm<sup>–1</sup>, 150(2) K, 16371 unique reflections [*R*(int) 0.0579], *R* (on *F*) 0.0556, *wR* (on *F*<sup>2</sup>) 0.1326 (*I* > 2 $\sigma$ *I*). CCDC 257099. See <http://www.rsc.org/suppdata/cc/b4/b417720g/> for crystallographic data in .cif or other electronic format.

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