Synthesis and X-Ray Crystal Structure of the First Homoleptic Main Group Diazadiene Complex, Bis(1,4-di-t-butyl-1,4-diazabuta-1,3-diene)gallium

F. Geoffrey N. Cloke,[*a] **Graeme R. Hanson,**[b] **Mark J. Henderson,**[c] **Peter B. Hitchcock,**[a] **and Colin L. Raston**[c]

[a] School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, U.K.
[b] Department of Chemistry, University of Queensland, St. Lucia 4067, Australia
[c] Division of Science and Technology, Griffith University, Nathan, Queensland 4111, Australia

Cocondensation of gallium vapour with 1,4-di-t-butyl-1,4-diazabuta-1,3-diene (Bu^{t}dab) affords the title compound as the first example of a homoleptic main group diazadiene complex; X-ray crystallography shows the molecule to possess distorted tetrahedral geometry, and together with e.s.r. and magnetic data suggests it to be a unique example of gallium(II) in which one of the diazadiene ligands has been doubly reduced.

Recently we described the metal atom synthesis of formally zero oxidation state homoleptic diazadiene complexes of titanium, yttrium, and some lanthanoid elements.[1] In this paper we report the synthesis and characterisation of the first homoleptic main group diazadiene complex.

Cocondensation of gallium vapour (generated from a resistively heated alumina crucible) with an excess of 1,4-di-t-butyl-1,4-diazabuta-1,3-diene (Bu^{t}dab) in toluene at 77 K yielded a deep green–brown solution after warm-up to room temperature. Removal of the solvent and excess of Bu^{t}dab (by sublimation), followed by low temperature recrystallisation of the residue from toluene–hexane afforded green–black crystals of [Ga(σ,σ-N,N′-Bu^{t}dab)$_2$], (1) (satisfactory microanalyses have been obtained), in ca. 20% yield (4.0 g) based on gallium. The analogous indium compound could not be prepared using the same method.

Compound (1) is moderately soluble in hydrocarbon solvents and air-sensitive, thermally stable (m.p. 190—193 °C without decomposition, under argon), and may be sublimed at ca. 150 °C and 10^{-4} mbar with partial decomposition; a parent ion with the appropriate gallium isotope pattern was observed in the mass spectrum. Compound (1) is paramagnetic, with μ_{eff} = 1.7 μ_B at 308 K (Evans' method[2]), and its e.s.r. spectrum in hexane shows coupling to nitrogen and gallium at room temperature [Figure 1(a)]. Computer simulation [Figure 1(b)] based on the two magnetic isotopes of gallium (60% ^{69}Ga, 40% ^{71}Ga, both $I = 3/2$) and four equivalent nitrogen atoms yields the following spin Hamiltonian parameters: $g_{av.}$ = 2.00238, A_{av}(Ga) = 18.39 × 10^{-4} cm^{-1} and A_{av}(N) = 2.638 × 10^{-4} cm^{-1}. The frozen solution spectrum at 130 K yields four gallium hyperfine resonances with nitrogen hyperfine coup-

ling unresolved, possibly because of a more complex coupling pattern arising from coupling to two pairs of magnetically distinct nitrogen atoms, viz an anisotropic metal environment. This is consistent with the structure of (1) in the solid state, which has been established by single crystal X-ray diffraction, and is shown in Figure 2 together with significant bond distances and angles.†
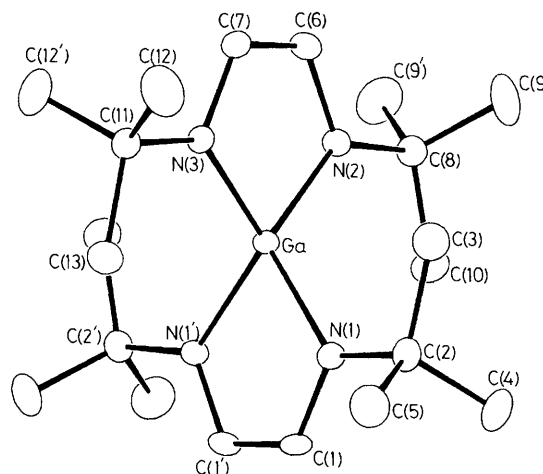

Figure 2. X-Ray crystal structure of (1). Selected bond lengths (Å): Ga–N(1), 1.864(4); Ga–N(2), 1.972(6); Ga–N(3), 1.966(5); N(1)–C(1), 1.395(6); N(2)–C(6), 1.331(9); N(3)–C(7), 1.321(9); C(1)–C(1′), 1.350(7); C(6)–C(7), 1.389(10). Selected angles(°): N(1)–Ga–N(1′), 90.4(2); N(2)–Ga–N(3), 84.9(2); N(1)–Ga–N(3), 121.3(2); N(1)–Ga–N(2), 121.3(1).
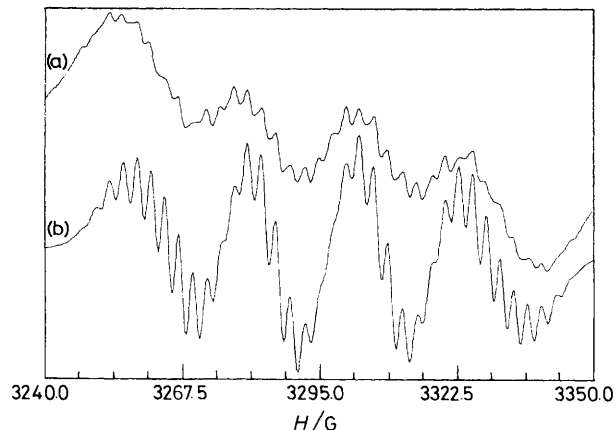
Figure 1. Experimental (a) and simulated (b) e.s.r. spectra of (1) (G = 10^{-4} T).
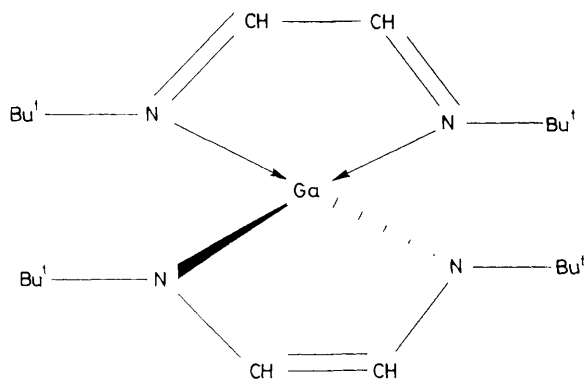
Figure 3. Bonding (1).

The molecule lies on a crystallographic mirror plane, the two planes defining the Bu^{t}dab ligands being mutually orthogonal, and exhibits distorted tetrahedral geometry around the central gallium atom. The average C=N and C–C bond lengths (1.326 and 1.389 Å respectively) in one of the Bu^{t}dab ligands in (1) are typical of those found in the transition metal analogues: for example [Mn(Bu^{t}dab)$_2$],[4] in which the corresponding bond lengths are 1.32 and 1.38 Å. However, the values for the other Bu^{t}dab ligand show significant deviations: the C=N distance has lengthened to 1.395 Å, with a corresponding reduction in the C–C distance to 1.350 Å. These changes are accompanied by a decrease in

Ga–N distance from 1.969 to 1.864 Å, and an increase in the 'bite angle' of the ligand from 84.9 to 90.4°.

Consideration of these results suggests that one of the Bu^{t}dab ligands has been reduced to Bu^t-N̄–CH=CH-N̄ -Bu^t, with concomitant oxidation of the metal centre to give a complex of, formally, gallium(II) as shown in Figure 3. This is confirmed by a magnetic moment which has the 'spin only' value for one unpaired electron, and an e.s.r. spectrum which shows coupling to both gallium and nitrogen. The reduction of the Bu^{t}dab ligand to give a metalladiazacyclopentene fragment may be compared with the extreme representation buta-1,3-diene–metal bonding as a metallacyclopentene.

References

1 F. G. N. Cloke, H. C. de Lemos, and A. A. Sameh, *J. Chem. Soc., Chem. Commun.*, 1986, 1344.
2 D. F. Evans, *J. Chem. Soc.*, 1959, 2005.
3 D. Kivelson, in 'Electron Spin Relaxation in Liquids,' eds. L. T. Muus and P. W. Atkins, Plenum Press, New York, 1972, pp. 213–277.
4 G. Van Koten and K. Vrieze, *Adv. Organomet. Chem.*, 1982, **21**, 152.