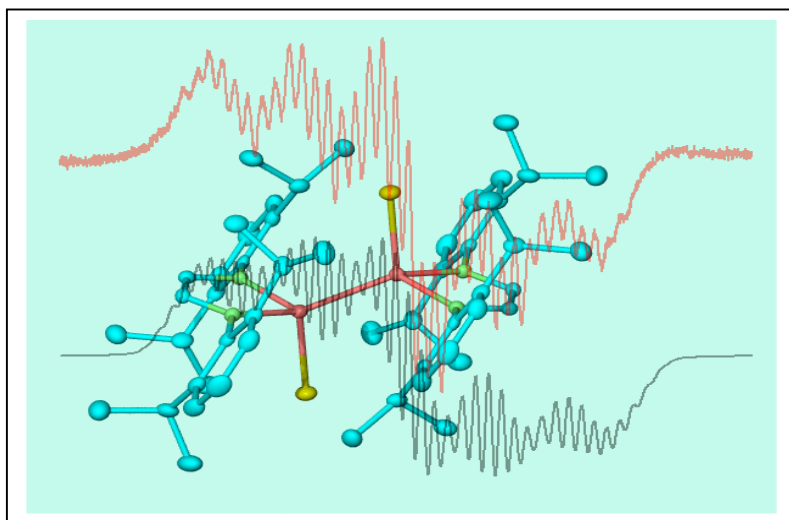


## An EPR and ENDOR investigation of a series of diazabutadiene-group 13 complexes

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Paramagnetic diazabutadiene-gallium(II or III) complexes,  $[(\text{Ar-DAB})_2\text{Ga}]$  and  $[\{(\text{Ar-DAB}^*)\text{GaX}\}_2]$  ( $\text{X} = \text{Br}$  or  $\text{I}$ ;  $\text{Ar-DAB} = \{\text{N}(\text{Ar})\text{C}(\text{H})\}_2$ ,  $\text{Ar} = 2,6$ -diisopropylphenyl), have been prepared by reactions of an anionic gallium N-heterocyclic carbene analogue,  $[\text{K}(\text{TMEDA})][:\text{Ga}(\text{Ar-DAB})]$ , with either "Gal" or  $[\text{MoBr}_2(\text{CO})_2(\text{PPh}_3)_2]$ . A related In(III) complex,  $[(\text{Ar-DAB}^*)\text{InCl}_2(\text{THF})]$ , has also been prepared. These compounds were characterised by X-ray crystallography and EPR/ENDOR spectroscopy. The EPR spectra of all metal(III) complexes incorporating the Ar-DAB ligand,  $[(\text{Ar-DAB}^*)\text{MX}_2(\text{THF})_n]$  ( $\text{M} = \text{Al}$ ,  $\text{Ga}$  or  $\text{In}$ ;  $\text{X} = \text{Cl}$  or  $\text{I}$ ;  $n = 0$  or  $1$ ) and  $[(\text{Ar-DAB})_2\text{Ga}]$ , confirmed that the unpaired spin density is primarily ligand centred, with weak hyperfine couplings to Al ( $a = 2.85\text{G}$ ), Ga ( $a = 17$ - $25\text{G}$ ) or In ( $a = 26.1\text{G}$ ) nuclei. Changing the N-substituents of the diazabutadiene ligand to *tert*-butyl groups in the gallium complex,  $[(^t\text{Bu-DAB}^*)\text{GaI}_2]$  ( $^t\text{Bu-DAB} = \{\text{N}(^t\text{Bu})\text{C}(\text{H})\}_2$ ), changes the unpaired electron spin distribution producing  $^1\text{H}$  and  $^{14}\text{N}$  couplings of  $1.4\text{G}$  and  $8.62\text{G}$ , while the aryl substituted complex,  $[(\text{Ar-DAB}^*)\text{GaI}_2]$ , produces couplings of *ca.*  $5.0\text{G}$ .



These variations were also manifested in the gallium couplings, *viz.*  $a_{\text{Ga}} \sim 1.4\text{G}$  for  $[(^t\text{Bu-DAB}^*)\text{GaI}_2]$  and  $a_{\text{Ga}} \sim 25\text{G}$  for  $[(\text{Ar-DAB}^*)\text{GaI}_2]$ . The EPR spectra of the gallium(II) and indium(II) diradical complexes,  $[\{(\text{Ar-DAB}^*)\text{GaBr}\}_2]$ ,  $[\{(\text{Ar-DAB}^*)\text{GaI}\}_2]$ ,  $[\{(^t\text{Bu-DAB}^*)\text{Ga}\}_2]$  and  $[\{(\text{Ar-DAB}^*)\text{InCl}\}_2]$ , revealed doublet ground states, indicating that the Ga-Ga and In-In bonds prevent dipole-dipole coupling of the two unpaired electrons. The hyperfine tensors for the imine protons, and the aryl and *tert*-butyl protons was obtained by ENDOR. In  $[(\text{Ar-DAB}^*)\text{GaI}_2]$ , gallium hyperfine and quadrupolar couplings were detected for the first time.