Supplementary information (ESI) for Dalton Trans.
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The supplementary material mainly contains some additional graphical information of the main part in order to visualize the arguments given there.

The figures 1’ – 17’ are presented on separate pages.
The corresponding figure captions are:

Fig. 1’: \( \text{Al}_4\text{Cp}^* \text{ and Ga}_6\text{Cp}^* \).
Fig. 2': \[ \text{Al}_2\text{Br}_4 \cdot 2\text{CH}_3\text{OC}_6\text{H}_5. \]
A: stainless steel vessel (30 L)
HV: high vacuum (~10-5 mbar)
D: solvent inject
B: Al in graphite container, heated resistively
C, K: heat shield and water cooling
HX: gaseous hydrogen halide
Lm/D: vaporized solvent/donor mixture
E: drain gutter
F: Schlenk vessel
G: Dewar vessel with dry ice (-78°C)

Fig. 3′: Apparatus for trapping e.g. the high-temperature molecule AlCl in a synthetic style.
Fig. 4: Metalloid clusters [Al\textsubscript{7}R\textsubscript{6}]\textsuperscript{−}, [Al\textsubscript{12}R\textsubscript{8}]\textsuperscript{−} and [Al\textsubscript{14}R\textsubscript{6}I\textsubscript{6}]\textsuperscript{2−} (R = N(SiMe\textsubscript{3})\textsubscript{2}).
Alₙ core of the metalloid clusters [Al₆₉R₁₈]³⁻ and [Al₇₇R₂₀]²⁻ (R = N(SiMe₃)₂). Ligand-bearing Al atoms are blue.
Fig. 6': The metalloid Al$_{50}$Cp$^*$$_{12}$ cluster: Al$_{38}$(AlCp$^*$)$_{12}$
Fig. 7': Section of the normal-pressure ($\alpha$, $\beta$, $\gamma$, $\delta$) and the high-pressure modifications (GaII, GaIII) of solid Ga. The fcc high-pressure modification GaIV is not shown.
Fig. 8': Cartoon in order to visualize the highly complex formation of the different Ga modifications from Ga subhalides via metalloid clusters as intermediates.
Fig. 9': $\text{Ga}_8\text{R}_6$ ($\text{R} = \text{C(SiMe}_3)_2$) as a prototype for a molecular metal-metal bond and its relation to $\alpha$-gallium.
Fig. 10': $\text{Ga}_{10}\text{Br}_{10}(4\text{-}\text{tert-}\text{butylpyridine})_{10}$ (left) and its relation to the structure of $\alpha$-gallium (right).
Fig. 11′: Metalloid Ga clusters and their relation to β- (left) and δ-Ga (middle, right).
left: Ga$_{12}$Br$_2$(PR$_2$)$_6$(CHPR$_4$)$_2$; middle: [Ga$_{22}${N(SiMe$_3$)$_2$)$_{10}$Br$_{10}$]$^{2-}$; right: Ga$_{12}$(C$_{13}$H$_9$)$_{10}$$^{2-}$.
Fig. 12': Metalloid cluster $[\text{Ga}_{51}(\text{PtBu}_2)_{14}\text{Br}_6]^{3-}$
Fig. 13: Calculated atomic volumes of centred \{Ga_{12}\} and \{Ga_{13}/Ga_{14}\} moieties in metalloid clusters, naked \{Ga_n\} clusters and Ga modifications.
Fig. 14': The naked Ga$_{23}$ cluster in different perspectives.
Fig. 15': The Ga$_{24}$ core of the Ga$_{24}$Br$_{22}$ cluster with its inner and outer Ga$_{12}$ icosahedron.
Fig. 16': $\text{Si(AlCl}_2)_4\cdot 4\text{Et}_2\text{O}$. 
Fig. 17': Solid state $^{71}$Ga NMR spectrum of the Ga$_{64}$ cluster compound (conducting region, *cf.* text) at different temperatures.