Supplementary information (ESI) for Dalton Trans. This journal is © The Royal Society of Chemistry 2008

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': $Al_4Cp_4^*$ and $Ga_6Cp_6^*$.







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 $(-78^{\circ}C)$

Fig. 3': Apparatus for trapping *e.g.* the high-temperature molecule AlCl in a synthetic style.



Fig. 4': Metalloid clusters $[Al_7R_6]^-$, $[Al_{12}R_8]^-$ and $[Al_{14}R_6I_6]^{2-}$ (R = N(SiMe_3)₂).



Fig. 5': Al_n core of the metalloid clusters $[Al_{69}R_{18}]^{3-}$ and $[Al_{77}R_{20}]^{2-}$ (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': Ga_8R_6 (R = C(SiMe_3)_2) as a prototype for a molecular metal-metal bond and its relation to α -gallium.



Fig. 10': $Ga_{10}Br_{10}(4$ -*tert*-butylpyridine)_{10} (left) and its relation to the structure of α -gallium (right).



Fig. 11': Metalloid Ga clusters and their relation to β - (left) and δ -Ga (middle, right). left: Ga₁₂Br₂(PR₂)₆(CHPR₄)₂; middle: [Ga₂₂{N(SiMe₃)₂}₁₀Br₁₀]²⁻; right: Ga₁₂(C₁₃H₉)₁₀²⁻.



Fig. 12': Metalloid cluster $[Ga_{51}(PtBu_2)_{14}Br_6]^{3-}$



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}^{-1} 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': $Si(AlCl_2)_4 \cdot 4Et_2O$.



Fig. 17': Solid state 71 Ga NMR spectrum of the Ga₈₄ cluster compound (conducting region, *cf.* text) at different temperatures.