

## Electronic Supplementary Information

The supplementary material mainly contains some additional graphical information from the main part in order to visualize the arguments given there.

The corresponding figure captions are:

Fig. 1':  $\text{SiAl}_{14}\text{Cp}^*_6$ : The  $\text{SiAl}_8$  core is surrounded by 6  $\text{AlCp}^*$  moieties.<sup>[1]</sup>

Fig. 2': The metalloid clusters  $[\text{Al}_7\text{R}_6]^-$  ( $\text{R} = \text{N}(\text{SiMe}_3)_2$ ) and  $[\text{Al}_7\text{R}_6]$  ( $\text{R} = \text{N}(\text{SiMe}_3\text{Ph})_2$ ) (only the Al, N and Si atoms are shown).<sup>[2, 3]</sup>

Fig. 3': The  $\text{Al}_{69}$  core of the metalloid clusters  $[\text{Al}_{69}\text{R}_{18}]^{3-}$ , ( $\text{R} = \text{N}(\text{SiMe}_3)_2$ ).<sup>[4]</sup>

Fig. 4': The  $\text{Al}_{12}(\text{AlX}_2)_{10}$  core of the halides  $\text{Al}_{22}\text{X}_{20} \cdot 12\text{D}$  ( $\text{X} = \text{Br}, \text{Cl}$ ;  $\text{D} = \text{THF}$ ).<sup>[5, 6]</sup>

Fig. 5': A central  $\text{Ga}_{12}$  icosahedron is surrounded by a second  $\text{Ga}_{12}$  icosahedron which is encapsulated by a  $\text{Br}_{18}\text{Se}_2$  pentagonal dodecahedron.<sup>[7]</sup>

Fig. 6':  $[\text{Ga}_{12}(\text{GaR} \cdot \text{Br})_{10}]^{2-}$ : A central  $\text{Ga}_{12}$  icosahedron is surrounded by 10 Br-bridged GaR units.<sup>[8]</sup>

Fig. 7':  $\text{Al}_{50}\text{Cp}^*_{12}$ : a core of  $[\text{Al}_8\text{Al}_{30}]$  is surrounded by 12  $\text{AlCp}^*$  moieties.<sup>[9]</sup>

Fig. 8': In the  $[\text{Ga}_{84}\text{R}_{20}]^{4-}$  cluster anion ( $\text{R} = \text{N}(\text{SiMe}_3)_2$ ), 64 naked Ga atoms ( $2 + 32 + 30$ ) are coordinated by 20  $\text{GaN}(\text{SiMe}_3)_2$  moieties.<sup>[10, 11]</sup>

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