

# Eclipsed- and Staggered-[Ge<sub>18</sub>Pd<sub>3</sub>{EiPr<sub>3</sub>}<sub>6</sub>]<sup>2-</sup> (E = Si, Sn): Positional Isomerism in Deltahedral Zintl Clusters

Perla L.G.

Muñoz-Castro A.

Sevov S.C.

We report the synthesis and characterization of the cluster anions [Ge<sub>18</sub>Pd<sub>3</sub>{SiiPr<sub>3</sub>}<sub>6</sub>]<sup>2-</sup> (1) with a core of face-fused twinned icosahedra, Ge<sub>18</sub>Pd<sub>3</sub>, and two sets of three iPr<sub>3</sub>Si-substituents positioned in "eclipsed" geometry. The new anion is a positional isomer of the recently reported "staggered" stannyl-ligated counterpart [Ge<sub>18</sub>Pd<sub>3</sub>{SniPr<sub>3</sub>}<sub>6</sub>]<sup>2-</sup> (2), showing the possibility to find such positional isomerism in Zintl clusters. Both anions are characterized by single-crystal X-ray diffraction, <sup>1</sup>H and <sup>13</sup>C NMR, and negative-ion ESI-MS. Using relativistic DFT calculations, we elucidate and discuss the reasons for the different positioning of the ligands in the stannyl- and silyl-functionalized species. © 2017 American Chemical Society.