An Icosahedral 55-Atom Iron Hydride Cluster Protected by Tri-*tert*-butylphosphines

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Nanoclusters are nanometer-sized molecular compounds characterized by significant metal–metal bonding and low average oxidation states, and they exhibit unique properties distinct from those of small metal complexes or nanoparticles.[1)] In contrast to the diverse range of sizes and structures discovered for coinage metal nanoclusters, the family of iron clusters remains limited to the subnanometer scale (i.e., <1 nm)[2)3)] owing to the relatively weak iron–iron bonds and the high reactivity of low oxidation state iron. Here, we report the characterization of a cationic 55-atom Fe nanocluster paired with an anionic 6-atom Fe cluster, formulated as $[Fe_{55}H_{46}(P^tBu_3)_{12}][Fe_6H_8\{N(SiMe_3)_2\}_6]$ (**[Fe$_{55}$][Fe$_6$]**)[4)].

[Fe$_{55}$][Fe$_6$] was synthesized from the reaction of $Fe\{N(SiMe_3)_2\}_2$ with HBpin in the presence of bulky P^tBu_3 in 13% yield. Single-crystal X-ray crystallography confirmed the structure of **[Fe$_{55}$][Fe$_6$]**. **[Fe$_{55}$]** has an icosahedral core with a diameter of 1.2 nm and the 12 vertices of the **Fe$_{55}$** icosahedron are occupied by P^tBu_3 ligands. In contrast, **[Fe$_6$]** displays an octahedral core with each Fe atom bound to a silylamide (i.e., $-N(SiMe_3)_2$) (Figure A). Electrospray ionization (ESI) mass spectrometric analysis was performed to determine the formulas, including the hydrides, of the **[Fe$_{55}$]** cation and the **[Fe$_6$]** anion. X-ray absorption fine structure (XAFS) analysis determined the average oxidation state of Fe in **[Fe$_{55}$][Fe$_6$]** (Figure C). Further characterization of **[Fe$_{55}$][Fe$_6$]** was carried out using other analytical techniques.

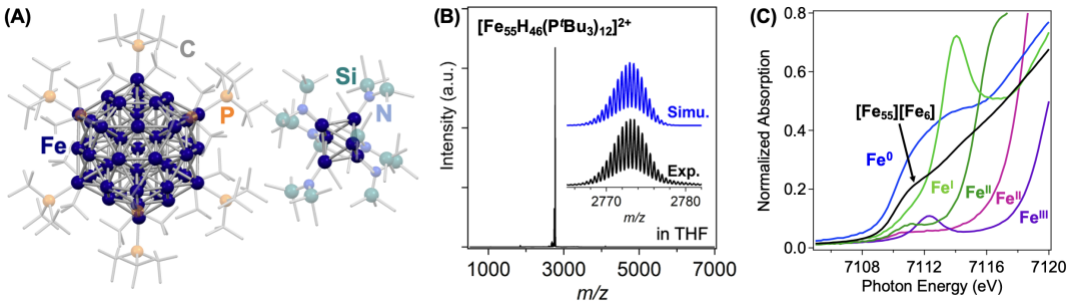

Figure. (A) Crystal structure, (B) Positive-mode ESI mass spectrum, and (C) Fe *K*-edge XANES spectrum of **[Fe$_{55}$][Fe$_6$]**. Reference samples for XAFS analysis: Fe^0 (blue) = Fe powder, Fe^I (light green) = $[K(18\text{-crown-}6)][Fe\{N(SiMe_3)_2\}_2]$, Fe^{II}(green) = $Fe\{N(SiMe_3)_2\}_2$, Fe^{II} (violet) = $FeCl_2$, Fe^{III} (purple) = $FeCl_3$.

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