

Counteraction Control of Metal- vs. Ligand-Centered Reduction in Cerium Complexes: Access to Formally Zerovalent Cerium

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Low-valent cerium chemistry remains challenging because highly reduced Ce species are often unstable and because redox-active ligands can compete with metal-centered reduction. Here, we show that these two reduction manifolds can be selectively accessed within a bis(acyl)phosphide-supported cerium platform by controlling the environment of the potassium counteraction. Starting from $[\text{Ce}^{\text{III}}(\text{MesBAP})_3(\text{THF})]$ (**1**), reduction with KC_8 in THF induces ligand redistribution and inner-sphere potassium coordination, yielding the dianionic $-\text{ate}$ complex $[\{\text{K}(\text{THF})\}_2\text{Ce}^{\text{II}}(\text{MesBAP})_4]$ (**2**). Structural, NMR, UV/vis, EPR, and SQUID magnetometric data establish this compound as a genuine, room-temperature-stable Ce(II) complex with magnetic properties consistent with a $4f^2$ electronic configuration.

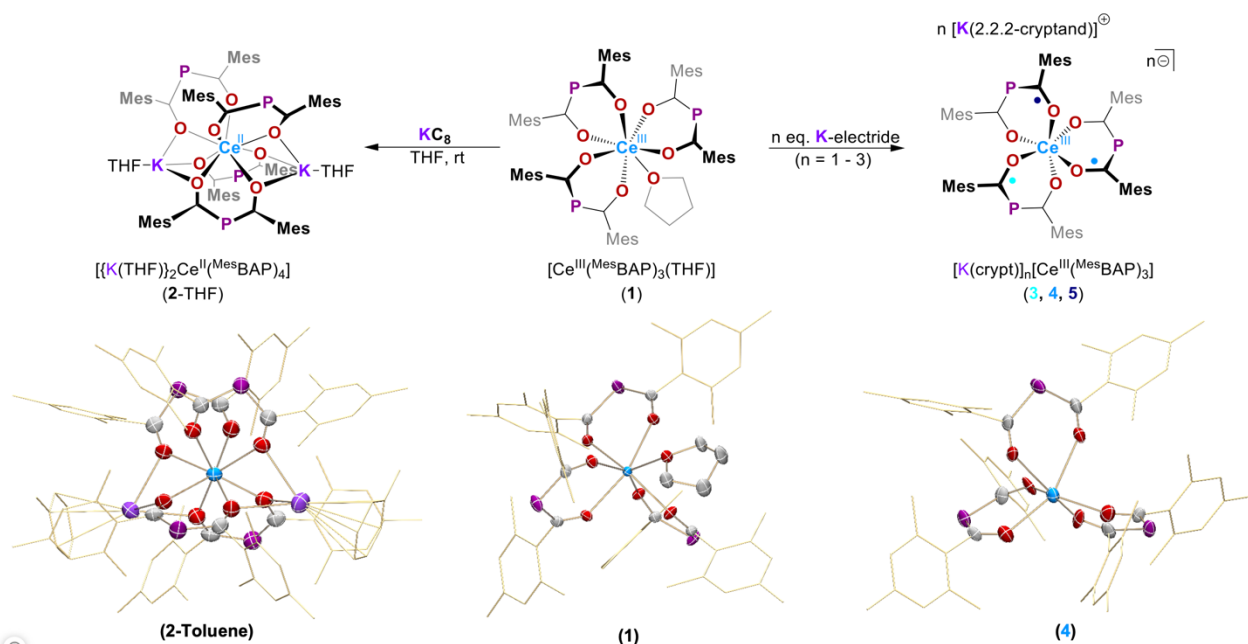


Fig. 1. Counteraction control of metal- versus ligand-centered reduction in $\text{Ce}^{\text{MesBAP}}$ complexes (top). Solid-state molecular structures of $[\{\text{K}(\text{toluene})\}_2\text{Ce}^{\text{II}}(\text{MesBAP})_4]$ (**2-Toluene**), $[\text{Ce}^{\text{III}}(\text{MesBAP})_3(\text{THF})]$ (**1**), and dianion of $[\text{K}(\text{2.2.2-crypt})]_2[\text{Ce}^{\text{III}}(\text{MesBAP})_3]$ (**4**).

In contrast, use of the soluble $\text{K}(\text{2.2.2-cryptand})$ electride preserves the 1:3 coordination environment and redirects reduction to the MesBAP ligands, affording $[\text{K}(\text{2.2.2-cryptand})]_n[\text{Ce}^{\text{III}}(\text{MesBAP})_3]$ with $n = 1-3$.

These complexes formally correspond to Ce(II), Ce(I), and Ce(0), but spectroscopic and magnetic analyses show that they retain $\text{Ce}^{\text{III}} f^1$ centers antiferromagnetically coupled to one, two, or three ligand-centered radicals. Notably, the trianionic member represents an unprecedented formally zerovalent cerium complex. In preliminary reactivity studies, the reduced complexes also react with CO_2 to form CO and K_2CO_3 ; for the Ce(II) $-\text{ate}$ species, reformation of the Ce(III) precursor closes a synthetic Ce(III)/Ce(II) cycle.

These results demonstrate that controlling counteraction coordination and encapsulation provides a powerful handle for switching the locus of reduction between the metal center and the ligand manifold in Ce-BAP chemistry.