

Exploiting Ligand Oxidation State: Cyanometallate Cages with Redox-Switchable Host/Guest Chemistry and Redox-Activation of Alkenes by Platinum Complexes with Non-innocent Ligands

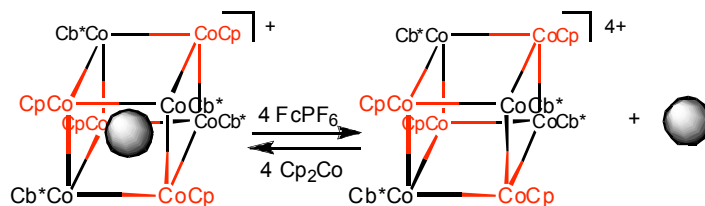
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Molecular coordination cages assembled with rigid linkers possess well-defined interior cavities. The interesting prospect of these ensembles is their capacity to serve as molecular containers; to date coordination cages have been exploited as catalysts,^{1,2} molecular sieves,³ sensors,⁴ and trapping reagents for reactive species.⁵ The family of supramolecules discussed herein are constructed from cyanide linkers. The rigid frameworks of cyanometallates impart size selective sieving capabilities.⁶ For example, the neutral molecular box $\{[\text{CpCo}(\text{CN})_3]_4[\text{Cp}^*\text{Ru}]_4\}$ displays an unparalleled preference for Cs^+ vs K^+ .⁷ Recent advances in the chemistry of molecular cyanometallates will be addressed, with an emphasis on the incorporation of functional subunits into these rigid molecular cages.

The condensation of the redox addressable $[\text{Cb}^*\text{Co}(\text{NCMe})_3]\text{PF}_6$ ($\text{Cb}^* = \text{C}_4\text{Me}_4$) with the tricyanide $[\text{Cp}^*\text{Rh}(\text{CN})_3]^-$ in the presence of alkali metals (M) generates electroactive cages of the general formula $\{\text{M} \llbracket [\text{Cp}^*\text{Rh}(\text{CN})_3]_4[\text{Cb}^*\text{Co}]_4 \rrbracket^+\}$ ($[\text{M} \llbracket \text{Rh}_4\text{Co}_4 \rrbracket^+$, $\text{M} = \text{K}^+$ or Cs^+). The analogous homometallic cages $\{\text{M} \llbracket [\text{CpCo}(\text{CN})_3]_4[\text{Cb}^*\text{Co}]_4 \rrbracket^+\}$ ($[\text{M} \llbracket \text{Co}_8 \rrbracket^+$) were prepared similarly via the condensation of $[\text{Cb}^*\text{Co}(\text{NCMe})_3]^+$ with $[\text{CpCo}(\text{CN})_3]^-$ in the presence of alkali metal cations. The redox addressable $\text{Cb}^*\text{Co}^{\text{I}}$ subunits of $[\text{M} \llbracket \text{Co}_8 \rrbracket^+$ cage enabled the tuning of the cyanometallate framework's charge and, consequently, control of the framework's host/guest chemistry (Scheme 1). Upon oxidation of $[\text{M} \llbracket \text{Co}_8 \rrbracket^+$, the encapsulated cation is expelled affording the empty $[\text{Co}_8]^{4+}$ cage. The $[\text{M} \llbracket \text{Co}_8 \rrbracket^+$ cage can be regenerated by the reduction of $[\text{Co}_8]^{4+}$ in the presence of alkali metal cations. The electroactive cages displayed voltammetric response for the encapsulated alkali metal cation.⁸

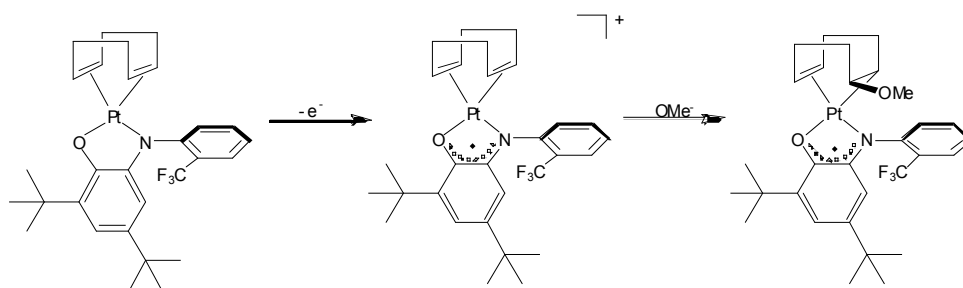


Scheme 1. Redox-switched complexation/decomplexation of K^+ and Cs^+ by molecular cyanometallate cages.

The second part of the talk focuses on the synthesis, characterization and reactivity of organometallic complexes with non-innocent ligands (NIL). While there are a multitude of reviews concentrating on the structural, magnetic, and electronic properties of M-NIL complexes,⁹⁻¹¹ far fewer reports on the reactivity of M-NIL complexes with important substrates have been communicated.¹²⁻¹⁴ These co-operating ligands act as electron reservoirs, absorbing or

supplying electrons during chemical transformations. Also, NIL centered redox changes alter the NIL's donor properties which affect the metal center and the other ligands.^{15,16}

Studies on the role of NILs in other areas of organometallic chemistry are accelerating.¹⁷⁻¹⁹ Despite these advances, the influence of redox poise of a NIL on alkenes remains underdeveloped. Alkene complexes with NIL have been described, but their redox congeners have not. In this work, the influence of the amidophenolate NILs on the coordination properties of alkenes is examined. Alkene complexes have broad importance, including economically significant processes such as Wacker oxidation along with innumerable stoichiometric processes.²⁰



Scheme 2. Alkene activation by oxidation of a non-innocent co-ligand.

A small family of Pt(NIL)(diene) complexes were generated by the treatment of PtCl₂(diene) with deprotonated catechol or aminophenol ligands. The complexes Pt(^tBA^FPh)(COD), Pt(^tBA^FPh)(nbd), and Pt(O₂C₆H₂^tBu₂)(COD) (H₂^tBA^FPh = 2-(2-trifluoromethyl)anilino-4,6-di-*tert*-butylphenol, O₂C₆H₂^tBu₂ = 3,5-di-*tert*-butylcatecholate) were examined using cyclic voltammetry (CV) to benchmark the influence of ^tBA^FPh²⁻ relative to standard catecholate ligands. And indeed the amidophenolate complexes were more easily oxidized (~350 mV) than the catecholate analogues. Treatment of Pt(^tBA^FPh)(COD) and Pt(^tBA^FPh)(nbd) with AgPF₆ afforded the imino-semiquinones [Pt(^tBA^FPh)(COD)]PF₆ and [Pt(^tBA^FPh)(nbd)]PF₆, respectively. Complexes [Pt(^tBA^FPh)(COD)]^{0/+} and [Pt(^tBA^FPh)(nbd)]^{0/+} represent the first examples of an alkene bound to an M-NIL complex in two redox states. The redox active character of the amidophenolate allowed us to “turn on” the electrophilicity of the coordinated alkene. Whereas Pt(^tBA^FPh)(COD) proved unreactive toward nucleophiles, the oxidized derivatives rapidly and stereospecifically add alkoxides at carbon (Scheme 2).

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