

## Early Transition Metal Clusters

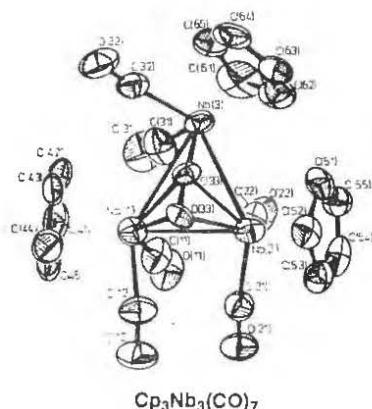
John Gozum

Literature Seminar

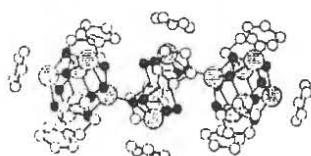
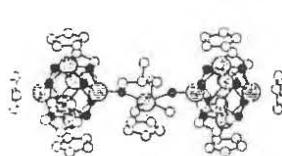
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Transition metal clusters have been intensively studied as potential catalysts or models for catalytic processes and have played an important role in the development of multicenter bonding models [1]. Most cluster complexes of the transition metals involve metals from the later groups, and by contrast, early transition metals clusters are relatively little studied. Such early d-block clusters present new challenges in understanding the bonding in electron deficient systems, and are accordingly of great interest. The reactivity of such species remains largely unexplored.

Few carbonyl clusters of the early transition metals have been reported. Thermal and photochemical syntheses are claimed for "Cp<sub>4</sub>V<sub>4</sub>(CO)<sub>4</sub>", "Cp<sub>3</sub>V<sub>3</sub>(CO)<sub>9</sub>", and Cp<sub>3</sub>Nb<sub>3</sub>(CO)<sub>7</sub>. While the vanadium complexes are not well characterized [2], the niobium complex has been shown to possess a unique bridging carbonyl ( $\nu_{CO} = 1330 \text{ cm}^{-1}$ ) that serves a formal six electron donor [3]. Variable temperature NMR studies of (MeCp)<sub>3</sub>Nb<sub>3</sub>(CO)<sub>7</sub> show that the bridging carbonyl undergoes a rapid fluxional exchange process.



Early organometallic transition metal clusters can also be stabilized by oxides and sulfides. Included in this family are octahedral Cp<sub>6</sub>Ti<sub>6</sub>O<sub>8</sub> [4], and paramagnetic Cp<sub>5</sub>V<sub>5</sub>O<sub>6</sub> [5]. Two structurally related compounds are Cp<sub>11</sub>V<sub>13</sub>O<sub>18</sub><sup>-</sup>(NMe<sub>3</sub>)<sub>2</sub> and Cp<sub>14</sub>V<sub>16</sub>O<sub>24</sub> which are formed in the reaction of Cp<sub>2</sub>V with Me<sub>3</sub>NO, and which consist of two Cp<sub>5</sub>V<sub>6</sub>O<sub>8</sub> clusters linked by bridging oxo vanadium units [6].

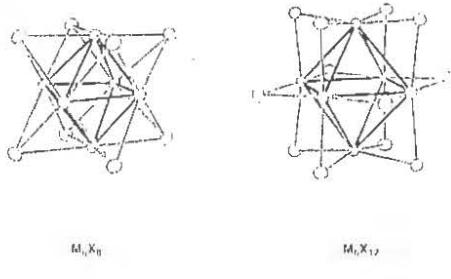


Sulfides stabilize clusters in a fashion similar to oxide ligands.  $\text{Cp}_5\text{Ti}_5\text{S}_6$  is structurally similar to  $\text{Cp}_5\text{V}_5\text{O}_6$  [7]. Electron deficient cubanes of the formula  $(\text{RCp})_4\text{M}_4\text{S}_4$  (where M = Ti, V) are known with total cluster electron counts ranging from 52 to 56 electrons [8].

Organometallic clusters of the early transition metals containing halide ligands are limited to the arene trimers of the general formula  $[\text{M}_3(\text{Me}_6\text{C}_6)\text{X}_6]^-$  where M = Ti, Zr, Nb, Ta and X is a halide [9]. These complexes are prepared by reducing a higher-valent metal halide with aluminum in the presence of the arene.

A number of inorganic clusters stabilized by oxides, sulfides and halides are known; the oxo trimer  $[\text{Nb}_3\text{O}_2(\text{O}_2\text{CMe})_6]^{5-}$  and the cyclic tetranuclear cluster  $[\text{Nb}_4\text{S}_2(\text{SPh})_{12}]^{4-}$  are examples of such species [10]. Inorganic halide trimers are represented by the paramagnetic  $\text{Nb}_3\text{X}_8$  type. These are generally synthesized by solid state reactions in sealed niobium or tantalum tubes. Diamagnetic  $\text{Nb}_3\text{Cl}_7(\text{PMe}_3\text{Ph})_6$  is made by the reduction of  $[\text{NbCl}_2(\text{THF})]_2\text{Cl}_2(\text{THT})$  with Na/Hg in the presence of the phosphine [11].

Inorganic halide hexamers are a large and important class of early d-block clusters, and can be divided into three general classes:  $\text{M}_6\text{X}_8$ ,  $\text{M}_6\text{X}_{12}$  and those with interstitial atoms. Representative of the  $\text{M}_6\text{X}_8$  type is the paramagnetic 19 electron cluster of  $\text{Nb}_6\text{I}_{11}$  which possess eight face-capping iodides; and six exo or outward pointing iodides each of which is shared with another  $\text{Nb}_6$  cluster [12]. The cluster reacts with  $\text{H}_2$  at temperatures greater than  $300^\circ\text{C}$  to give the 20 electron diamagnetic cluster,  $\text{Nb}_6\text{I}_{11}\text{H}$  [13]. The  $\text{Nb}_6\text{I}_{11}$  cluster can also be reduced to form  $\text{CsNb}_6\text{I}_{11}$  (20 electrons),  $\text{CsNb}_6\text{I}_{11}\text{H}$  (21 electrons), and  $\text{Nb}_6\text{I}_8-(\text{NH}_2\text{R})_6$  (22 electrons) [14].



Examples of the  $\text{M}_6\text{X}_{12}$  class are best found in  $\text{Ta}_6\text{I}_{14}$  and related compounds in which two of the edge-bridging halides occupy the axial exo position of another clusters [15].

The first early transition metal halide cluster with an interstitial atom was  $\text{Nb}_6\text{I}_{11}\text{H}$ ; the next reported discovery was 15 years later when  $\text{Zr}_6\text{I}_{14}\text{K}$  was described [16]. Further experiments and recalculation of data led to reformulation of the previously reported  $\text{Zr}_6\text{I}_{14}$  clusters as interstitial carbides of stoichiometry  $\text{Zr}_6\text{I}_{14}\text{C}$ , the source of carbon being uncertain [17]. The effect of incorporating an interstitial carbon is to raise the electron count by four electrons per cluster. In subsequent years, a plethora of interstitial atoms ranging from main group elements to transition metals have been placed in the

centers of  $Zr_6X_{12}$  type clusters [18]. Analysis of the  $Zr_6I_{14}E$  type cluster unit cell volumes vs. ionic radii suggest that the reported  $Zr_6I_{14}K$  compound should be reformulated.

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