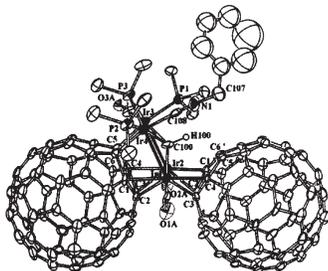


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### Two Metal Centers Bridging Two $C_{60}$ Cages as a Wide Passage for Efficient Interfullerene Electronic Interaction

G. Lee, Y.-J. Cho, B.K. Park, K. Lee, and J.T. Park, *J. Am. Chem. Soc.* 125 (2003) 13920.



Studies of the coordination of  $C_{60}$  to various metal centers have shown that  $C_{60}$  can adopt a number of  $\sigma$ - and  $\pi$ -type bonding modes. In the above communication,  $C_{60}$  was reacted with a tetrahedral iridium cluster to give a product containing the four iridium centers in a planar geometry with two  $C_{60}$  ligands. Two of the iridium centers bridge both  $C_{60}$  ligands, with the other iridium centers bridging only one. The electronic properties of this complex were investigated by cyclic voltammetry using a BASi 100B. The cyclic voltammogram showed three pairs of redox processes, consistent with sequential, pairwise addition of six electrons into the  $C_{60}$  ligands. However, the separation of the processes within each pair shows that there is significant electronic interaction between the two  $C_{60}$  ligands, which was attributed to the metal bridge between the ligands.

### The Standard Redox Potential of the Phenyl Radical/Anion Couple

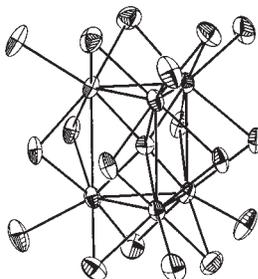
C.P. Andrieux and J. Pinson, *J. Am. Chem. Soc.* 125 (2003) 14801.

The aim of this study was to measure the redox potential of the phenyl radical by generating the radical *in situ* by reduction of a series of aryldiazonium cations. The cyclic voltammograms of these cations showed one large

reduction peak due to the reduction of the aryldiazonium cation, and a second, much smaller, reduction peak due to the reduction of the phenyl radical generated by the initial reduction. It was proposed (based on simulations performed using DigiSim<sup>®</sup>) that the initial addition of an electron to the aryldiazonium cation was concerted with the cleavage of the C-N bond; that is, the phenyl radical was generated in a single step. It was also demonstrated that the small size of the second reduction peak was consistent with the phenyl radical being involved in a competing reaction, which in this case was a proton transfer reaction. The redox potential of the phenyl radical was calculated from thermodynamic and kinetic parameter values obtained using DigiSim.

### New Routes to Transition Metal-Carbido Species: Synthesis and Characterization of the Carbon-Centered Trigonal Prismatic Clusters $[W_6CCl_{18}]^{n-}$ ( $n = 1, 2, 3$ )

E.J. Welch, N.R.M. Crawford, R.G. Bergman, and J.R. Long, *J. Am. Chem. Soc.* 125 (2003) 11464.

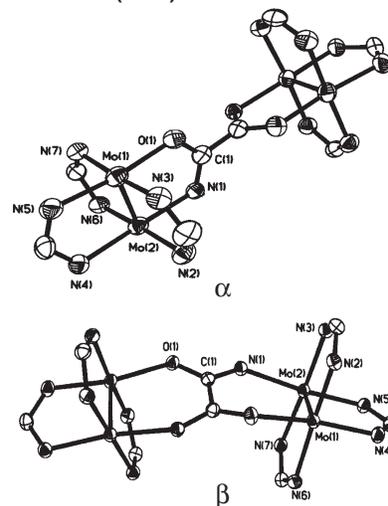


This article discusses electronic properties of  $[W_6CCl_{18}]^{2-}$ , determined by cyclic voltammetry using a CV-50W and molecular orbital (MO) calculations. The cyclic voltammogram showed two reductions and two oxidations. This observation was consistent with the MO calculations, which showed many closely-spaced orbitals in the frontier orbital region. The HOMO had  $a_2''$  symmetry, but the LUMO could not be unambiguously assigned, since there were low-lying unoccupied  $e'$  and  $e''$  orbitals of similar energy. On the basis of the cyclic voltammetry data, the monoanion was

generated by the addition of 1 equivalent of  $NO^+$ , and the trianion by the addition of 1 equivalent of cobaltocene. The molecular structures of the three anions ( $n = 1, 2,$  and  $3$ ) were obtained using X-ray crystallography, and structural changes were correlated with orbital properties derived from the MO calculations. Upon oxidation of the dianion, there is no change in the  $D_{3h}$  symmetry, but the triangular W-W distances increase, and the other W-W distances decrease. This is consistent with a HOMO that is W-W bonding within the W triangles, but anti-bonding along the other W-W edges, and this pattern was indeed observed in the  $a_2''$  HOMO generated by the MO calculations. In contrast, the trianion showed significant distortion from  $D_{3h}$  symmetry, consistent with a Jahn-Teller distortion caused by population of one of the low-lying unoccupied  $e'$  orbitals.

### Modifying Electronic Communication in Dimolybdenum Units by Linkage Isomers of Bridged Oxamidate Dianions

F.A. Cotton, C.Y. Liu, C.A. Murillo, D. Villagrán, and X. Wang, *J. Am. Chem. Soc.* 125 (2003) 13564.



This is one in a series of papers that examine the tetrametallic compounds formed by reaction of bimetallic molecular complexes with linking molecules. In this study, bimolybdenum complexes were reacted with oxamidate anions, and two isomeric

tetramolybdenum complexes were produced. These isomers differed in the relative orientations of the bimetal units. In the  $\alpha$  isomer, these units were essentially perpendicular, whereas in the  $\beta$  isomer, they were parallel. The redox properties of both isomers were studied by cyclic voltammetry using a BASi 100. Each isomer showed two redox couples, but the separation of couples was much larger for the  $\beta$  isomer. This was attributed to the greater electronic interaction possible in the  $\beta$  isomer due to the better orbital overlap allowed by the parallel geometry.

**Experimental and Theoretical Study of the Activity of Substituted Metallophthalocyanines for Nitrite Electro-Oxidation**

C.A. Carlo, F. Bedioui, M.A. Paez, G.I. Cardenas-Jiron, and J.H. Zagal, J. Electrochem. Soc. 151 (2004) E32.

The basis of this article was the electrocatalytic oxidation of nitrite by various metallophthalocyanines. A range of different complexes were used that varied in the nature of the metal center and the substituents on the phthalocyanine ring. The electrocatalytic activity was investigated by cyclic voltammetry (using a BASi

100B/W) and rotating disk voltammetry. It was shown that the rate and the mechanism varied with the nature of the complex. The nitrite coordinated to either the metal center or the peripheral ligand, depending upon the electrophilicity of the metal center (metal centers with a formal +3 oxidation state being more electrophilic than metal centers with a formal +2 oxidation state). The rate of the catalytic mechanism was faster for those complexes where the nitrite coordinated to the metal center, and electron-donating substituents on the ligand also increased the rate of reaction. However, none of these variations were particularly pronounced, and this was attributed to a relatively weak interaction between nitrite ion and the complex.

**Redox Chemistry of Actinide Ions in Wells-Dawson Heteropolyoxoanion Complexes**

M.-H. Chiang, L. Soderholm, and M.R. Antonio, Eur. J. Inorg. Chem. (2003) 2929.

Polyoxometalates are inorganic, anionic ligands that can undergo multiple reduction reactions, and hence their electrochemical properties have been studied in great detail. In this article, one  $\text{WO}^{4+}$  unit of the Wells-Dawson heteropolyanion,  $\alpha$ -

$[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ , was substituted by a number of actinide cations  $\text{An}^{n+}$  to yield a series of  $\alpha\text{-}[\text{An}^{n+}(\alpha\text{-2-P}_2\text{W}_{17}\text{O}_{61})_2]^{n-20}$  complexes, the redox properties of which were investigated by cyclic voltammetry using a BASi 100B/W. Of particular interest was the possibility of interaction between heteropolyanion and actinide orbitals of similar energy. Oxidations were observed for the  $\text{Am}^{3+}$  and  $\text{U}^{4+}$  complexes, which were attributed to oxidation of the actinide cation. All the complexes undergo multiple reductions, as does the uncomplexed heteropolyanion. Of the five actinides studied, only  $\text{Np}^{4+}$  and  $\text{Pu}^{4+}$  can be reduced in the available potential window, but comparison of the cyclic voltammograms of the complexes and the uncomplexed heteropolyanion showed that the reductions of the heteropolyanion was modulated by coordination. Since the actinide reductions occurred in the same potential windows as the heteropolyanion reductions, the redox potentials of the actinide reductions and the number of electron transferred ( $n$ ) were derived from Nernst plots based on X-ray absorption spectroelectrochemistry. For  $\text{Np}^{4+}$ , the value of  $n$  was 1, but a value of 0.72 was calculated for  $\text{Pu}^{4+}$ . This low value was attributed to delocalization of electrons between the actinide and anion orbitals.