

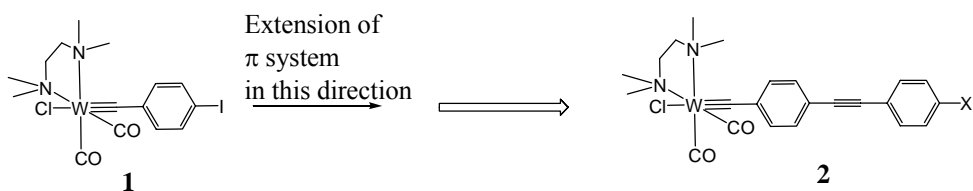
Report on USB-BNL Research Initiative Grants 1999 and 2000

Metal-Carbon Multiple Bonds as Building Blocks for Molecular Electronic Devices

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The research conducted with the support of the USB-BNL research initiative focused on the development of *metal-carbon multiple bonds as functional and structural components in molecular materials*. The expectation that metal-carbon multiple bonds will be of practical use in these roles is based on two fundamental properties, namely the strong electronic coupling between transition metal atoms and unsaturated organic systems, which is established by metal-carbon π bonds, and the well-defined coordination geometries characteristic of transition metal complexes. This combination of electronic and steric properties provides a potentially powerful basis for the design of electron-active molecular materials.

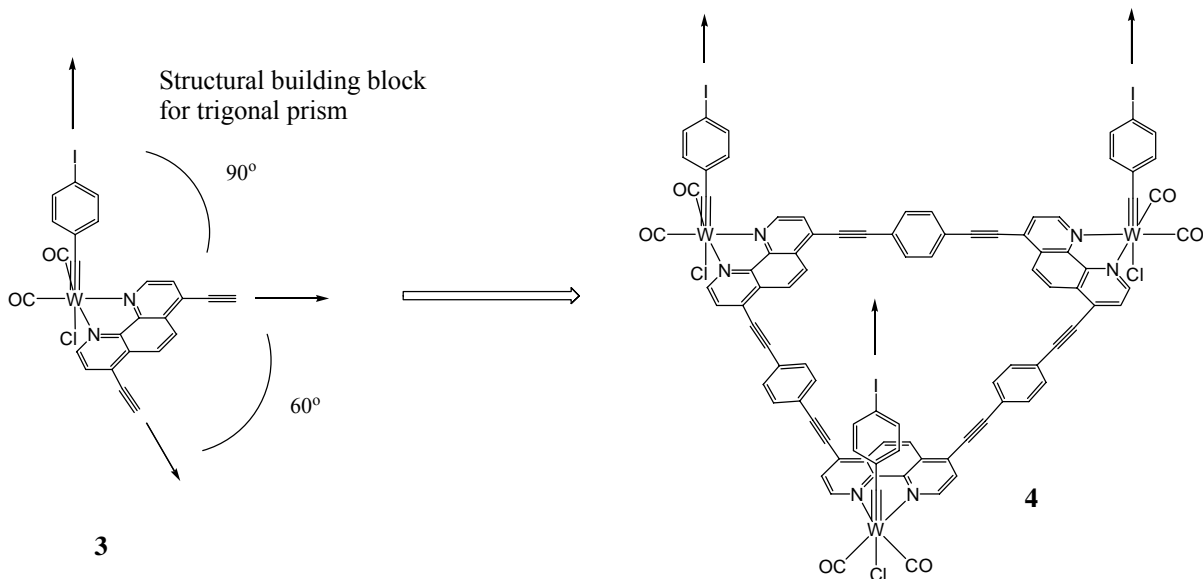
Specifically, it was the goal of the funded effort to synthesize molecular systems that contain metal-carbon triple bonds in electronic conjugation with extended unsaturated organic systems. We prepared several tungsten benzylidyne complexes of the type **1**. These compounds contain a tungsten-carbon triple bond connected to a phenyl ring. The phenyl ring bears an iodine group that provides an opportunity to extend the π system by adding ethynylphenylene groups to afford compounds of the type **2**. This is accomplished by adding ethynylene and phenylene groups through sequential palladium-catalyzed coupling reactions.



Compounds **2** were intended for studies of electron-transfer events between the tungsten center (W) and the terminal functional group (X). Dr. Bruce Brunschwig is an expert in electron transfer chemistry. His intended role in the collaboration was the investigation of the intramolecular electron transfer properties of compounds **2**. However,

while our synthetic work was in progress he moved to the California Institute of Technology. This aspect of the project was then no longer pursued.

In order to test metal alkylidyne complexes as structural building blocks in molecular materials, we prepared compound **3**. Compound **3** is a tungsten alkylidyne complex that also contains a special phenanthroline ligand. As indicated in the drawing, the phenanthroline ligand can be extended in two “horizontal” directions, with a 60° angle between them. At the same time, the alkylidyne ligand can be extended in the “vertical” direction. Thus, the possibility exists to construct molecular trigonal prisms.



By attaching functional side chains along the edges, the molecular 3-D frameworks can be modified in different ways. Thus they have many potential applications. For example, the frameworks could be used to hold clusters inside the open cavity. Such enclosed clusters could then be placed between nanofabricated electrodes to serve as single-electron devices. This potential application establishes a direct connection to our ongoing collaboration with Prof. Konstantin K. Likharev in the area of molecular electronics. It was exploited as the basis for a successful NSF-NER grant application entitled “Caged Clusters for Single-Electronics”. Our efforts on the synthesis of 3-D molecular frameworks are still ongoing. The work has not yet been published.

After the departure of Dr. Brunschwig from BNL, I have established contacts with Dr. John Miller and Dr. Ben Ocko to establish a new collaborative SBU-BNL effort. This new work is focusing on the electronic and surface assembly properties of long unsaturated organic molecules such as those used as the edges of the 3-D molecular frameworks. As soon as the molecular 3-D frameworks become available, they will also be subject to collaborative investigations.