

Organometallic Molecular Wires

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It has been recognized for many years that molecular wires have potential uses in molecular scale analytical devices. Initially, research was focused on organic compounds with conjugated π -electron networks,¹ in which discrete organic molecules with chains up to 128 Å in length have been reported.² Recently, organometallic chemists have actively sought to incorporate metal centers into these conjugated π -electron networks.

Organometallic molecular wires consist of two redox-active terminal metal centers bridged by a ligand that promote the exchange of an electron between the two metals. Linear (sp) carbon chains have been investigated as potential bridges because of their π -interactions. Currently, linear bridged organometallic wires have been synthesized with sp carbon chains ranging from 1-20 carbons in length and having metal centers with varying electronic configurations.³⁻⁴ Stable compounds of both homo-metallic and hetero-metallic complexes have been synthesized. Specific examples include the use of iron by Lapinte and co-workers,⁵ manganese by Berke and co-workers,⁶ and iron, platinum, rhenium and manganese by Gladysz and co-workers.⁷⁻⁹ Currently, the longest linear carbon chain complex to be crystallized is the di-platinum C₁₆ complex by Gladysz and co-workers (Figure 1).⁹

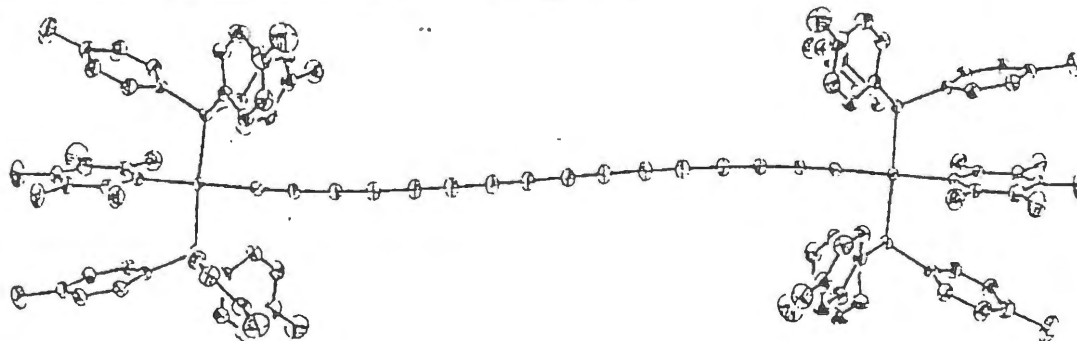


Figure 1

The synthetic procedures developed for carbon bridging complexes depend on whether the number of carbons is even or odd. Synthesis of the even carbon chain compounds has been readily achieved by the use of copper-catalyzed oxidative coupling of a polyynyl complex ($M-(C\equiv C)_n-H$).⁹ Odd carbon chain compounds are less common and require more sophisticated synthesis strategies such as carbon chain extension using one and two carbon precursors and carbon chain degradation using larger even carbon chain compounds.¹⁰

Certain properties of these compounds characterize them as molecular wires. Most have two reversible one-electron oxidations. Stable species with different oxidation states for these compounds have been isolated and characterized. Also, these compounds tend to have Class III mixed valence characteristics with the odd electron being fully delocalized over the whole molecule.¹¹ Many have large potential energy differences (ΔE) between oxidations, large comproportionation constants (K_c), and high electronic

coupling parameters (V_{ab}). All of which give an indication of how well the metal centers are communicating and the stability of the mixed valence complexes.

Organometallic chemists have also focused on how the electrochemical properties of these complexes change with varying chain length and ligands. Gladysz and co-workers¹²⁻¹³ and Sgamellotti and co-workers¹⁴ have intensely studied the effects of increasing chain length on oxidation potentials and found that as the chain lengthens, the oxidation potentials become less favorable and the comproportionation constants and HOMO-LUMO gap decrease. Bruce and co-workers¹⁵ and Lapinte and co-workers¹⁶ investigated the effects of different ligands (donating vs. accepting) and found that oxidation is thermodynamically more favorable for compounds that have electron-donating ligands on the metal centers.

Linear bridged organometallic wires have the ability to transfer electrons from one metal center to the next but are not ready for industrial use. The next step in research is to build longer chain bridges that are capable of easily transferring electrons, which may be done by varying the metals and ligands used in these complexes. After synthesizing the desired complexes, then developing an efficient way to connect the wire to a macroscopic interface has to be addressed before any large scale testing can occur.

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