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An Iron-Capped Metal−Organic Polyyne: $\{[Fe](C\equiv C)_2[W]\equiv CC\equiv CC\equiv [W](C\equiv C)_2[Fe]\}$

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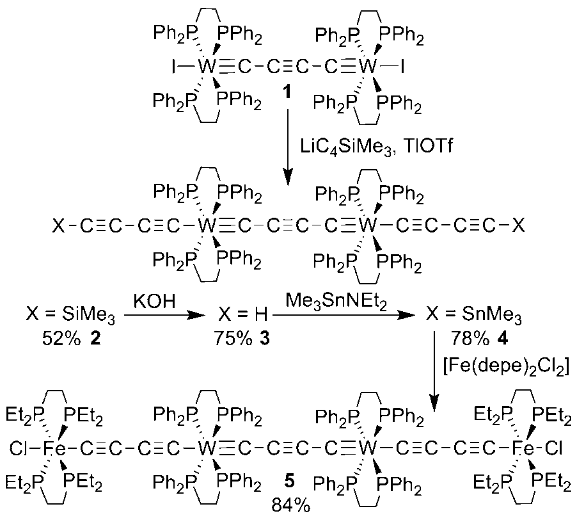
One of the long-standing fundamental challenges in the field of molecular electronics is the accomplishment of nanometer-sized low-resistivity rigid-rod-type molecules.[1] Compounds bearing redox-active metal ends seemed particularly suited for high single-electron conductivity, and one approach to enhanced conductivity, termed the “relay” approach, was based on the idea that higher rates of electron transfer between the remote ends could eventually be accomplished by creating linked sections of alternating metal centers and short bridges of “conducting” organic moieties.[2] In contrast to organic single-electron-conducting molecules, metal-containing redox wires are expected to possess low work functions and strong d_π/p_π interactions, allowing the metal centers to become intrinsic constituents of the electronic conjugation.[3,4] We reasoned that organometallic p_π/d_π-conjugated complexes of the type $\{H(C\equiv C)_n[M]\equiv C(C\equiv C)_nC\equiv [M](C\equiv C)_nH\}$[5] constitute unique building blocks for the construction of polymetallic “molecular wires”, and on the basis of a tungsten compound with the given structural motif, we approached the preparation of a tetranuclear polyyne of the type $\{[Fe](C\equiv C)_2[W]\equiv C(C\equiv C)C\equiv [W](C\equiv C)_2[Fe]\}$. Such systematic build-up of oligomers can also afford tunable systems for the development of bulk-conductive, nonlinear optical, luminescent, and magnetic materials.[4,6,7]

Scheme 1. Reaction Path for **1**−**5**



Our first preparative goal was to achieve access to the $\{(HC_4)[W](C_4)[W](C_4H)\}$ polyyne. The starting material utilized for this approach was the $[I(dppe)_2W(C_4)W(dppe)_2I]$ complex [**1**, dppe = 1,2-bis(diphenylphosphino)ethane] obtained recently in our group.[8] A controlled way of substituting the iodide ligands was the key to further functionalization of this dinuclear complex. Quite strong tungsten−iodine bonds combined with the possibility for trans → cis rearrangement rendered all standard strategies unsuccessful. The conversion of **1** to **2** was eventually achieved using a 3-fold excess of a 1:1 mixture of TlOTf with $LiC\equiv CC\equiv CSiMe_3$ in the presence of a catalytic amount of copper iodide (Scheme 1; also see the Supporting Information). The mechanism of this transformation is unclear, but it seems reasonable to infer the involvement of a putative Tl(III) intermediate formed by disproportionation of the unstable Tl(I) acetylide to metallic thallium as one of the observed reaction products. The desired product $[(Me_3SiC_4)(dppe)_2W(C_4)W(dppe)_2(C_4SiMe_3)]$ (**2**) was separated by low-temperature chromatography on alumina followed by crystallization from ether in 52% yield. Complex **2** was fully characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy, and its structure was confirmed by X-ray diffraction (XRD) analysis (see the Supporting Information). Removal of the $SiMe_3$ protecting group was achieved using excess KOH in a mixture of THF, methanol, and water. The desilylated compound $[(HC_4)(dppe)_2W(C_4)W(dppe)_2(C_4H)]$ (**3**) is stable in both solution and the solid state in the absence of light and oxygen.

X-ray structural analysis of **3** revealed a biscarbyne-type bridged $[(dppe)_2W\equiv C(C\equiv C)C\equiv W(dppe)_2]$ moiety coupled with C_4H chains (Figure 1). The crystal structure shows alternation of the W≡C and C≡C triple bonds and W−C and C−C single bonds, affirming that the bridge can be viewed to consist of a ditungstenatetradecaheptayne unit analogous in structure to the $HC_{14}H$ parent compound. Introduction of the tungsten fragments makes the compound much more stable than any polyyne H_2C_n ($n > 4$) molecule. **3** was converted to the corresponding stannylated derivative $[(Me_3SnC_4)(dppe)_2W(C_4)W(dppe)_2(C_4SnMe_3)]$ (**4**) via reaction with excess Me_3SnNEt_2 in order to obtain a stable precursor with controllable reactivity.

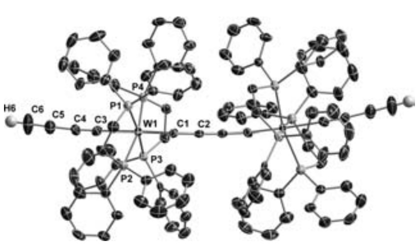


Figure 1. Thermal ellipsoid plot of the structure of **3** (50% probability level).

Finally, we wanted to perform preliminary investigations on the suitability of the $\{(C\equiv C)_2[W]\equiv C(C\equiv C)C\equiv [W](C\equiv C)_2\}$ building block for electron transfer. For this purpose, the conjugated bridge had to be capped with redox-active groups. An iron-containing group was chosen as the terminal metal center on the basis of the fast electron transfer observed earlier in dinuclear FeC_nFe systems.[9] Indeed the $[Fe(PP)_2X]$ fragment (PP = chelate phosphine; X =

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halogen) allows reversible redox properties to be combined with the possibility of further functionalization by halogen substitution for the attachment of anchor groups,[6,10,11] a key requirement for single-molecule conductivity measurements.[12] On the basis of our previous work, the reaction of **4** with [Fe(depe)$_2$Cl$_2$] [depe =1,2-bis(diethylphosphino)ethane] was carried out at 60 °C, giving {[Cl(depe)$_2$Fe]C$_4$[(dppe)$_2$W]C$_4$[W(dppe)$_2$]C$_4$[Fe(depe)$_2$Cl]} (**5**) in 84% yield after 6 h. Compound **5** is stable in the solid state and solution in the absence of air. **5** consists of a bridging {(C≡C)$_2$[W]≡C(C≡C)C≡[W](C≡C)$_2$} fragment essentially identical in structure to **3** that is end-capped with [Fe(depe)$_2$Cl] units (Figure 2). The added iron units induce an S-shaped distortion of the ditungstenatetradecaheptayne axis from linearity, with the main deviations from 180° at the C$_\alpha$ atoms of the tungsten centers being similar to other complexes with polyyne bridges.[8,13] The Fe−Fe distance in **5** is 23.5 Å.

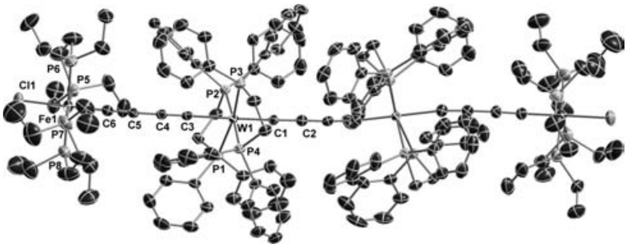

Figure 2. Thermal ellipsoid plot of the structure of **5** (50% probability level).

The redox properties of **5** were evaluated by cyclic voltammetry (CV) in dichloromethane (Figure 3) and THF (see the Supporting Information). The assignment of redox waves to oxidation processes was based on the fact that the oxidation potentials of **1** are higher than those for the iron in [Cl(depe)$_2$Fe(C$_2$R)]-type complexes.[11] As a consequence, the first two oxidation waves belong to the iron centers. The stabilization of the mixed-valence complex in dichloromethane solution is reflected by a peak separation of $\Delta E = 188$ mV with a comproportionation constant (K_c) of 1500.

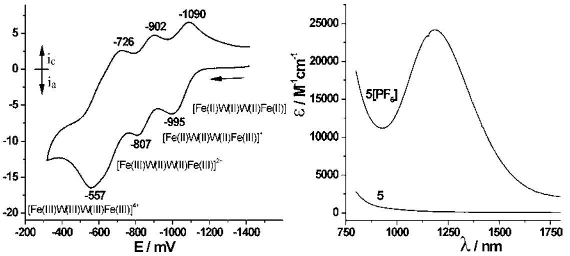

Figure 3. (left) Cyclic voltammogram of **5** in 0.1 M [*n*Bu$_4$N][PF$_6$] (Au electrode; *E* vs Fc$^{0/+}$; scan rate =100 mV/s; 20 °C; CH$_2$Cl$_2$). (right) NIR spectrum of **5[PF$_6$]** in CH$_2$Cl$_2$ solution. The background spectrum of **5** is shown for comparison.

On the basis of electrochemical studies, **5** was oxidized with 1 equiv of [Fe(Cp)$_2$][PF$_6$] in dichloromethane solution to give the mixed-valence complex **5[PF$_6$]**. The communication between the iron centers was additionally probed by IR, near-IR (NIR), and electron paramagnetic resonance (EPR) studies (Figure 3; also see the Supporting Information). The mixed-valence complex **5[PF$_6$]** shows a strong Gaussian-shaped band in the NIR spectrum. Data were analyzed using the Hush approximation.[14] It results in electronic coupling energy (H_{ab}) of 680 cm^{-1}, implying that the electron transfer should be described by an adiabatic regime with an estimated rate constant on the order of 10^9 s^{-1}.[15] The EPR spectra show a relatively sharp signal with $g = 2$ at both room and liquid helium temperatures. Moreover, only weak anisotropy was noticed for the resonance in frozen solution. This could be the result of partial delocalization of the electron into the ligands due to the covalent nature of the bonds.[16] However, the IR spectrum of **5[PF$_6$]** shows additional ν(C≡C) absorptions relative to **5**, suggesting localization of the unpaired electron on the IR time scale and favoring the Hush approximation.

In summary, we have developed long linear tungsten complexes with a continuous conjugated system. This building block efficiently mediates communication between two metal centers over a 24 Å distance, as shown by investigation of the tetranuclear complex **5** with redox-active termini. Fast electron transfer in combination with reversible oxidation of all four metal centers, the presence of terminal reactive sites for further functionalization, and the suitability for surface attachment because of its cylindrical shape and stability makes **5** a unique and promising system for long-range electron transfer, particularly in the field of metal-based molecular wires. This work shows great potential for the development of organometallic d$_\pi$/p$_\pi$-conjugated materials in general. In particular, further functionalization of **3** and **5** by anchor groups could lead to an investigation of single-molecule conductivity in these oligonuclear complexes; that investigation is currently in progress.

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Supporting Information Available: Synthesis of all compounds; details of single-crystal X-ray diffraction studies; CIF files; thermal ellipsoid plot of **2**; EPR, CV, and IR data for **5[PF$_6$]**; and detailed analysis of NIR, IR, and EPR data. This material is available free of charge via the Internet at http://pubs.acs.org.

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