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Pentalene Complexes of Group 7 Metal Carbonyls: An Organometallic Mixed-Valence System with Very Large Metal−Metal Electronic Coupling

Simon C. Jones,[†] Tony Hascall,[†] Stephen Barlow,[‡] and Dermot O'Hare*[,†]

Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, OX1 3QR, U.K., and
Department of Chemistry, University of Arizona, Tucson, Arizona 85721

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Complexes in which two or more metal centers are simultaneously coordinated to a bridging ligand are of interest due to the possibility of a variety of electronic interactions between the metal centers, and as models for organometallic polymers.[1] The fused-ring 8π-ligand pentalene (Pn = C_8H_6) is known to facilitate strong coupling between metal centers in the series of bimetallic complexes: *anti*-[M(η^5-C_5Me_5)](μ:η^5:η^5-Pn)[M′(η^5-C_5Me_5)] (M = M′ = Fe, Co, Ni, Ru; M = Fe, M′ = Co, Ru).[2] However, the use of pentalene as a ligand in organometallic chemistry[3] remains relatively unexplored in comparison to that of other bridging ligands; this may be ascribed in part to the difficulty involved in the synthesis of precursors to the pentalene dianion, the starting point for most pentalene chemistry. Here we report on the synthesis of the first group 7 carbonyl derivatives of pentalene, their redox chemistry, and the character of a highly delocalized mixed-valence derivative.[4]

Reaction of Li_2Pn with 2 equiv of $Mn(CO)_3(py)_2Br$ in THF gives, after workup, an orange solid. A single-crystal X-ray structure shows this to be the 34-electron complex *anti*-$[Mn(CO)_3]_2$(μ:η^5:η^5-Pn), **1** (Figure 1), in which the two organometallic fragments are η^5-coordinated to opposite faces of an essentially planar pentalene ring. Infrared spectroscopy reveals two CO stretching bands (ν_{CO} = 2006, 1922 cm^{-1}), consistent with local C_{3v} symmetry for the two equivalent $[Mn(CO)_3]$ units.

The analogous reaction of Li_2Pn with 1 equiv of $[Re(CO)_3(THF)Br]_2$ in THF gives a mixture of isomers of yellow *anti*-$[Re(CO)_3]_2$(μ:η^5:η^5-Pn) (**2**) and white *syn*-$[Re(CO)_3]_2$(μ:η^5:η^5-Pn) (**3**). The two isomers were separated by fractional crystallization. As with **1**, both **2** and **3** are diamagnetic.

The crystal structure of **3** (Figure 2) reveals a nonplanar pentalene ring system, bent away from the metal centers. The Re−Re distance is 3.23 Å, longer than that in $Re_2(CO)_{10}$ (3.04 Å),[5] suggesting no significant direct M−M bonding. The infrared spectra of **2** and **3** in the carbonyl stretching region are also very different − two bands are seen in **2** (ν_{CO} = 2013, 1913 cm^{-1}), while **3** has four bands (ν_{CO} = 2038, 1998, 1960, 1906 cm^{-1}), indicating some coupling of the CO vibrations of the $[Re(CO)_3]$ units in the syn-isomer.[6] The relative yields of **2** and **3** are temperature dependent, the percentage of **2** in the mixture increasing with increasing reaction temperature. NMR experiments show that, once formed, isomers **2** and **3** are not interconverted at temperatures up to 100 °C. No evidence for a syn-isomer of **1** has been found, the difference between Mn and Re perhaps being due to the dimeric nature of the Re starting material.

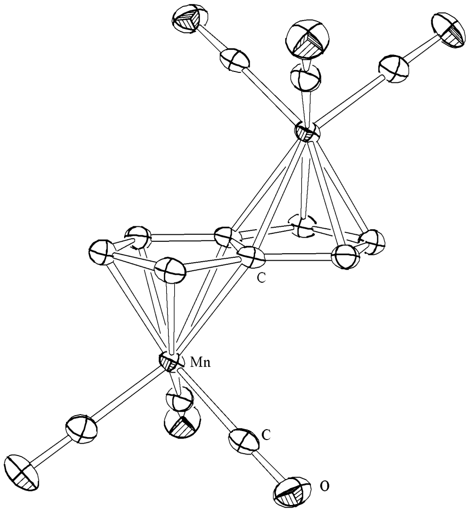

Figure 1. Crystal structure of **1** (ORTEP diagram, thermal ellipsoids at 50% probability, H atoms omitted for clarity).

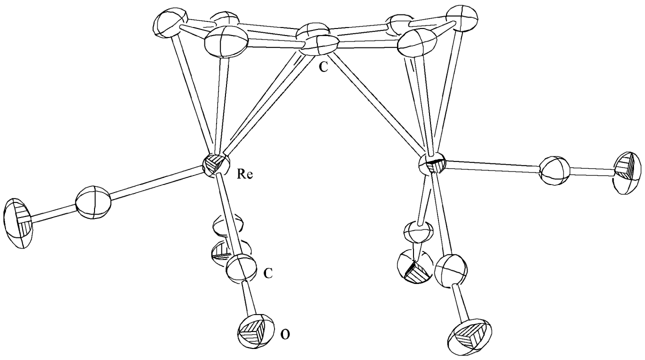

Figure 2. Crystal structure of **3** (ORTEP diagram, thermal ellipsoids at 50% probability, H atoms omitted for clarity).

While **2** and **3** display irreversible reductions (E_{red} = −3.22 and −2.67 V, respectively, vs ferrocenium/ferrocene, THF/0.1 M $Bu_4N^+PF_6^-$, 50 mV s^{-1}), the cyclic voltammogram of **1** shows two quasi-reversible[7a] waves at $E_{1/2}$ = −1.91 and −2.32 V, corresponding to reduction of **1** to [**1**]$^-$ and [**1**]$^{2-}$ respectively. The redox behavior of **1** is significantly different from that of Mn(η^5-C_5H_5)$(CO)_3$, which displays an irreversible reduction wave at −2.98 V in THF.[7b] Clearly this bimetallic complex does not behave like two separate $[Mn(CO)_3]$ units; the two metals interact strongly via the pentalene π-system, greatly stabilizing the reduced forms of **1**. The peak separation ($\Delta E_{1/2}$) for **1** is 410 mV, smaller than that between the two oxidations in the series *anti*-[M(η^5-C_5Me_5)]$_2$(μ:η^5:η^5-Pn) (M = Fe, Co, Ni); a value of $\Delta E_{1/2}$ = 710 mV is observed for the isoelectronic Co redox system in the same solvent.[2] **1**, [**1**]$^-$, and [**1**]$^{2-}$ are isoelectronic with the dicationic, monocationic, and neutral

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* To whom correspondence should be addressed. E-mail: dermot.ohare@chem.ox.ac.uk.
[†] University of Oxford.
[‡] University of Arizona.

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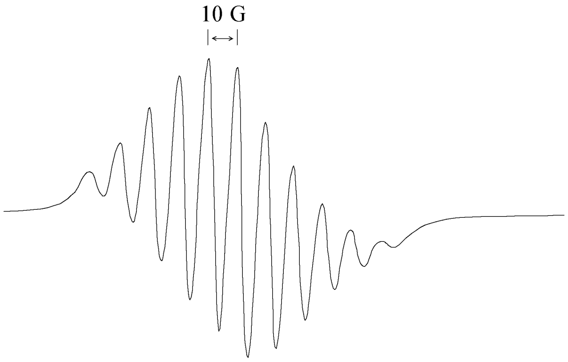

Figure 3. EPR spectrum of [**1**]$^-$ in THF at room temperature.

dicobalt species, respectively. However, no simple relationship between electronic coupling, *V*, and $\Delta E_{1/2}$ exists, and the unreliability of estimating electronic interactions from $\Delta E_{1/2}$ data has recently been noted.[8]

Complex **1** reacts with excess potassium-graphite (KC_8) in THF to give a very air-sensitive purple solid, $K^+{}_2$[**1**]$^{2-}$, which is oxidized rapidly in the presence of air or water to **1**; the salt is diamagnetic and has been characterized by ^{1}H NMR and IR spectroscopy, although its instability has precluded further characterization. $K^+{}_2$[**1**]$^{2-}$ has two CO stretching bands in its infrared spectrum (ν_{CO} = 1886, 1750 cm^{-1}), the reduced frequencies as compared to **1** being consistent with greater electron density on the metal centers in the dianion.

The green monoanion [**1**]$^-$, formally a Mn^I/Mn^0 mixed-valence species, can be formed by the reaction of **1** with 1 equiv of sodium naphthalenide in THF, although the solid decomposes rapidly upon attempted isolation, or by electrochemical reduction in THF or MeCN. It was successfully isolated through use of Fe(η^5-C_5H_5)(η^6-C_6Me_6)[9] as the reducing agent, although the [Fe(η^5-C_5H_5)(η^6-C_6Me_6)]$^+$[**1**]$^-$ salt is still very air-sensitive, being readily oxidized to **1**.

As expected, [**1**]$^-$ is paramagnetic; an EPR (X-band) spectrum was obtained in THF at room temperature (Figure 3). The 11-line pattern ($\langle g \rangle = 2.00$) results from hyperfine coupling to two equivalent ^{55}Mn centers ($I = {}^5/_2$), indicating that the rate of electron exchange between the two metal centers of [**1**]$^-$ is considerably greater than 3×10^7 s^{-1}. The hyperfine coupling constant (10 G) is small, suggesting the SOMO has significant ligand character. [Fe(η^5-C_5H_5)(η^6-C_6Me_6)]$^+$[**1**]$^-$ displays only two CO stretching bands (ν_{CO} = 1895 (sh), 1852 cm^{-1}) in its infrared spectrum, these values being intermediate between those observed for **1** and $K^+{}_2$[**1**]$^{2-}$. The observation of only two CO stretches shows that the two metal centers of [**1**]$^-$ are equivalent on the infrared time scale; the rate of intramolecular electron transfer must be considerably in excess of 10^{12} s^{-1}. The lowest energy electronic transition in the UV−vis−NIR spectrum (190−3000 nm) of [**1**]$^-$ in MeCN peaks at 781 nm (12 800 cm^{-1}) and can be assigned to intervalence charge transfer (IVCT). The band-width at half-height ($\Delta\nu_{1/2}$ = 2810 cm^{-1}) is much less than that predicted by Hush theory for the IVCT band of a class II mixed-valence system (for ν_{max} = 12 800 cm^{-1}, a $\Delta\nu_{1/2}$ value of 5440 cm^{-1} is predicted).[10] Furthermore, the energy of this transition does not vary significantly with solvent polarity (12 660 cm^{-1} in THF).

The IR spectrum and the characteristics of the UV−vis−NIR absorption discussed above suggest that [**1**]$^-$ belongs to class III (corresponding to two completely equivalent Mn$^{0.5}$ centers) in the Robin and Day classification of mixed-valence species,[11] or at least to class II−III (the so-called "solvent delocalized" régime in which the rate of electron exchange is much faster than that of solvent reorientation).[12] Interpretation of the vis−NIR spectra of **1** and its isoelectronic Co analogue,[2] under the assumption that they are class III species, gives the electronic coupling between the metal centers, $V = \nu_{IVCT}/2$, as 6400 and 4770 cm^{-1}, respectively. The value of *V* for [**1**]$^-$ is, to the best of our knowledge, the largest reported for a hydrocarbon-bridged bimetallic mixed-valence species[13] and approaches that found in the most delocalized class III organic mixed-valence systems (compare, for example, the values of 6890 and 8140 cm^{-1} found for *V* in the radical cations of *N*,*N*′-dimethyl-1,5-dihydrophenazine and *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine in MeCN).[14]

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Supporting Information Available: Full characterization data for all compounds (PDF) including crystal data for **1** and **3** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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