The Synthesis and Characterization of Bis(fulvalene)dimolybdenum and Its Monocarbonyl Adduct

Sir:

Recent interest in the structure and bonding of bis(fulvalene)dimetal complexes,[1] and our interest in the catalytic properties of coordinatively unsaturated derivatives, has led us to explore synthetic routes to complexes of the early transition metals.

We wish to report the synthesis of bis(fulvalene)dimolybdenum (**1**) and its monocarbonyl adduct, bis(fulvalene)dimolybdenum monocarbonyl (**2**). The synthesis of **1** utilized an in situ preparation of the bicyclopentadienide or fulvalene dianion,[2] followed by reaction with molybdenum(II) acetate to yield the dinuclear complex as a slightly soluble, dark red, air-sensitive solid. This thermally stable compound was purified[3] by vacuum sublimation at 250 °C.

Magnetic susceptibility measurements on solid samples from 4 to 300 K indicate that **1** is diamagnetic. The ^{1}H NMR spectrum of **1** exhibited two widely spaced areas[4] of resonance (tetrahydrofuran-d_8 δ 4.22, 6.45) for protons of the bridging fulvalene ligand, analagous to those observed for bis(fulvalene)diiron(II, II),[5] bis(fulvalene)dicobalt(III, III) dication,[6] and (η^5:η^5-fulvalene)hexacarbonyldimolybdenum(*Mo*–*Mo*).[2d] The large chemical shift difference between protons α and β to the bridge seems to be associated with a relatively coplanar disposition of five-membered rings. Both the ^{1}H NMR and infrared spectra[7] of **1** support its formulation as a dinuclear complex of D_{2h} point group symmetry.

Although the exact mode of ligand bonding and the degree of metal–metal bonding in this complex are presently unknown, two extremes warrant discussion. If substitution of molybdenum(II) acetate occurs without lowering the order of its quadruple bond, as has been found in tetrallyldimolybdenum[8] and the octamethyldimolybdate(II) ion,[9] then the fulvalene ligand may bond in a bis(biallyl) manner as a bridging η^3:η^3-ligand. Alternatively, if the fulvalene moiety bonded as an η^5:η^5-bridging ligand and a relatively coplanar disposition of five-membered rings were maintained, the metal–metal distance would be approximately 4.0 Å.[7] The observed diamagnetism could then be attributed to either an increase in d-orbital splitting to yield a 16 electron, $e_2{}^4$ configuration for each molybdenum, or to direct metal–metal exchange[1c] (bonding) or ligand propagated exchange.[1d,2c] Some intermediate geometry involving slippage of metal atoms from the pseudo-fivefold axis of the rings[7b] or bending of the bridge between rings[10] might easily allow for a metal–metal double bond and a closed shell configuration.

In reactions with π-acceptor ligands, **1** behaves as a Lewis acid. Carbon monoxide at 20 atm reacts with **1** to yield a slightly soluble, air sensitive, red-brown monocarbonyl adduct,[11] **2**. In tetrahydrofuran solution, **2** exhibits one sharp metal carbonyl stretch at 1735 cm^{-1}. The ^{1}H NMR spectrum at 360 MHz of **2**, in Figure 1, exhibits three widely spaced areas of resonance with well-resolved fine structure. The resonances at highest field consist of two multiplets separated by 0.05 ppm, which exhibit splittings that are similar to the symmetrical five- and six-line patterns of the resonances at lower field. Homonuclear spin-decoupling experiments clearly show the spectrum to be that of a completely coupled ABCD spin system, with coupling constants ranging from 2.9 to 0.8 Hz. In the absence of detailed structural information and possible magnetic anisotropy introduced by metal–metal bonding[12] as well as the complexity of cross-ring coupling in unsaturated five-membered rings,[13] no assignment of the spectrum is offered at this time. However, both the ^{1}H NMR and infrared spectra are consistent with a structure of C_{2v} symmetry shown in Figure 1, in which there are four symmetry related sets of nonequivalent protons for each η^5-ring, a metal–metal bond, and a symmetrically bridging carbonyl. Alternatively, some form of asymmetric bridging carbonyl may be present in a system undergoing rapid intramolecular exchange.

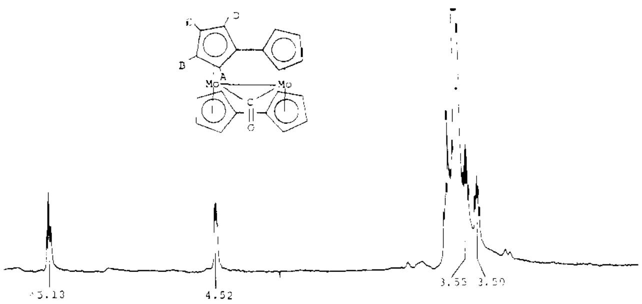

Figure 1. The 360-MHz ^{1}H NMR spectrum of bis(fulvalene)dimolybdenum monocarbonyl in 99% tetrahydrofuran-d_8. The large peak marked*, and the shoulder at *lower* field are solvent resonances.

Further synthetic and structural studies are underway in an effort to define the unique aspects of metallofulvalene complexes, compared to their "parent" metallocenes.

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References and Notes

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(3) Anal. Calcd for $C_{20}H_{16}Mo_2$: C, 53.59; H, 3.60; Mo, 42.81. Found: C, 53.61; H, 3.61; Mo, 42.90.

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