

This was confirmed by an X-ray structure determination.²³ The molecular structure of **4'** is shown in Figure 1. The fluorenylidene group is essentially perpendicular to the Mo=Mo bond and symmetrically bridges it (within 3 σ). The Mo=Mo distance is 2.798 (1) Å, a value approximately midway between the Mo-Mo triple and single bond distances in **1** and Cp₂Mo₂(CO)₆ (2.448 (1) and 3.235 (1) Å, respectively).^{24,25} Metal-Metal distances in compounds with formal Mo=Mo double bonds range from 2.486 to 2.885 Å with an average distance of 2.65 ± 0.12 Å (14 values).²⁷⁻³³ With the sole exception of **4**, these Mo=Mo complexes contain two or more bridging atoms, and the diverse nature of these groups accounts in large part of the wide range in Mo=Mo distances.

A fragment molecular orbital analysis (EHMO method)²⁶ has been made for a CH₂ model of **4**. Although there is a formal Mo-Mo triple bond ($\sigma^2\delta^2\delta^*\pi_{yz}^2\pi_{xz}^2$); (Figure 2) in the Cp₂Mo₂(CO)₄ fragment with the same structural parameters as found in **4**, a population analysis shows that only the σ and π_{xz} orbitals contribute substantially to metal-metal bond formation. Addition of the bridging CH₂ group lowers the Mo-Mo overlap population from 0.46 in the Cp₂Mo₂(CO)₄ fragment to 0.21 in Cp₂Mo₂(CO)₄(μ -CH₂), **4a**, by shifting the π_{xz} contribution from M-M bonding to M-(μ -CH₂) bonding, leaving the σ bond as the main contributor (71%) to M-M bonding. These results illustrate the problems associated with the assignment of formal metal-metal bond orders in low-symmetry systems.

The EHMO results have also been extremely useful in explaining the reactivity of **3** and **4**. Compound **4** does not react with CO (49 atm, 55 °C, 12 h), whereas **3** reacts rapidly (1 atm, 25 °C) to give Ph₂C=C=O and Cp₂Mo₂(CO)₆.⁵ At first glance, this reactivity order is rather surprising since **4** is formally unsaturated whereas **3** is not. A simplified explanation is afforded by the results in Figure 2. In **4a**, the CH₂ fragment lies along the -x axis and interacts strongly with the π_{xz} and π_{xz}^* orbitals as shown. This leaves a large gap (1.4 eV) between the LUMO and HOMO—the LUMO is a poor acceptor orbital and does not bind CO.

On the other hand, the CH₂ fragment in **3a** (Figure 2) is bonded along the -y axis, and it is the π_{yz} and π_{yz}^* orbitals that are split out, leaving a small gap (0.45 eV) between HOMO and LUMO. Furthermore, the LUMO is largely localized on one Mo atom and is ideally hybridized to bond to the Ph ring as actually found in **3** or to bond an additional CO ligand.

Recent kinetic data for the reaction of **3** with CO are consistent with a preequilibrium step in which the coordinated Ph group in **3** is detached to give a reactive intermediate, e.g., **3a**, which then binds the CO.³⁴ Thus, both the structure of **3** and the kinetic data are consistent with the MO picture which places a low-energy acceptor orbital on the μ -alkylidene structure, **3a**.

These analyses will be expanded in a future publication,³⁵ but

(23) Crystallized from toluene/hexane at 0 °C; $a = 11.716$ (5) Å, $b = 12.152$ (6) Å, $c = 17.488$ (4) Å, $\beta = 108.77$ (3)°, $Z = 4$, $V = 2358$ Å³, space group $P2_1/n$. Final residuals: $R_1 = 0.029$ $R_2 = 0.040$ on the basis of 3148 reflections with $I \geq 3\sigma(I)$.

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already these results have led to a better understanding of the factors influencing the reactivity of μ -alkylidenes and have emphasized that the presence of formal metal-metal multiple bonds, per se, does not confer enhanced reactivity on molecules containing them.

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Registry No. **1** (R = C₅H₅), 56200-27-2; **1'** (R = C₅H₄Me), 69140-73-4; **4**, 85957-07-9; **4'**, 85957-08-0; 9-diazo fluorene, 832-80-4.

(35) Additional points to be addressed include reasons for the different solid-state structures of **3** and **4**, their solution fluxionality, and the effects of the carbonyl geometries on the electronic structure and reactivity.

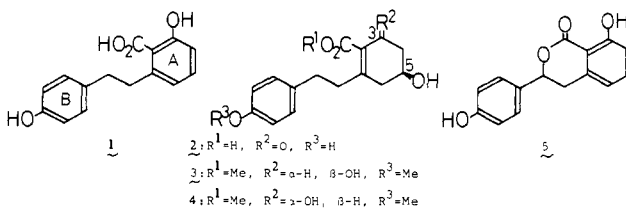
Prelunularic Acid, a Probable Immediate Precursor of Lunularic Acid. First Example of a "Prearomatic" Intermediate in the Phenylpropanoid-Polymalonate Pathway

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A naturally occurring stilbene carboxylic acid, lunularic acid (LNA, **1**), was isolated as a dormancy factor from a liverwort,



Lunularia cruciata, of Israel strain¹ and was proved to be identical with a growth regulator found in another liverwort, *Marchantia polymorpha*, in 1964.² Biosynthesis of LNA (**1**) has been shown to follow the phenylpropanoid-polymalonate pathway by radiolabeling techniques.³ Formation of ring A from three acetic moieties via a hypothetical β -triketo acid could be catalyzed by a stilbenecarboxylate synthase.⁴ However, no intermediates supposed to be formed in this biosynthetic process have so far been detected for LNA or for any other stilbenoids.

During the course of our studies on the bioformation of LNA (**1**) in suspension-cultured cells of *M. polymorpha*,⁵ we noticed the presence of a labile compound that gave LNA (**1**) on treatment under acidic or basic conditions. In this communication we report the isolation and structure determination of prelunularic acid **2**, which could be the direct precursor of LNA (**1**).

The cells of *M. polymorpha* (80 g fresh weight) cultured 14 days in a modified Murashige-Skoog medium^{6,7} containing 2% glucose and 1 mg/mL (2,4-dichlorophenoxy)acetic acid were harvested by filtration and extracted with 90% methanol. After

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