Metal-Metal Multiple Bonds. 16.1 Synthesis, Structure, and Reactivity of a Dimetallacyclopropene, $Cp_2Mo_2(CO)_4(\mu-C_{13}H_8)(Mo=Mo)^{\dagger}$

John J. D'Errico and M. David Curtis*

Department of Chemistry, The University of Michigan Ann Arbor, Michigan 48109 Received March 21, 1983

Compounds containing bridging alkylidene groups² are currently receiving considerable attention because of their possible role in catalytic processes.²⁻¹⁶ Complexes in which the alkylidene group bridges a metal-metal multiple bond are especially interesting since these unsaturated complexes may exhibit a different reactivity than their saturated analogues.

Several dimetallacyclopropenes (1) have been synthesized, most commonly by decarbonylation of dimetallacyclopropanes.^{2,8,16} In all cases a carbonyl ligand bridges the metal-metal bond of the resulting dimetallacyclopropene. Since it is well-known that the assignment of bond order to metal-metal bonds is complicated by the presence of bridging ligands,¹⁷⁻²⁰ it is most desirable to have a benchmark structure for unbridged dimetallacyclopropenes. We here report the first such structure, the preparation of which also represents the first actualization of the prototypal reaction 1.²¹



Our synthesis was patterned after our observation that diphenyldiazomethane reacts with $Cp_2Mo_2(CO)_4$ (1) as in eq 2



 $(M=Mo(CO)_2Cp)^5$ The final product, 3, contains a coordinated phenyl group and a Mo-Mo single bond. We reasoned that if the two phenyl rings were "tied back", then the resulting ste-

- (1) (a) Part 15: Shiu, K.-B.; Curtis, M. D.; Huffman, J. C. Organo-metallics, in press. (b) Part 14: Gerlach, R. F.; Duffy, D. N.; Curtis, M. D. *Ibid.* in press. (c) Part 13: D'Errico, J. J.; Messerle, L.; Curtis, M. D. *Inorg.* Chem. 1983, 22, 849.
- (2) Herrmann, W. A. Adv. Organomet. Chem. 1982, 20, 160.
 (3) Dyke, A. F.; Knox, S. A. R.; Mead, K. A.; Woodward, P. J. Chem. Soc., Chem. Commun. 1981, 861.
- (4) Herrmann, W. A.; Bauer, C.; Kriechbaum, G.; Kunkely, H.; Ziegler, M. L.; Speth, D.; Guggolz, E. Chem. Ber. 1982, 115, 878.
- (5) Messerle, L.; Curtis, M. D. J. Am. Chem. Soc. 1980, 102, 7789.
 (6) Messerle, L.; Curtis, M. D. J. Am. Chem. Soc. 1982, 104, 889.
- (7) Clause, A. D.; Shapley, J. R.; Wilson, S. R. J. Am. Chem. Soc. 1981, 103, 7387.
- (8) Theopold, K. H.; Bergman, R. G. J. Am. Chem. Soc. 1983, 105, 464, (9) Summer, C. E., Jr.; Collier, J. A., Pettit, R. Organometallics 1982, 1, 1350
- (10) Thorn, D. L.; Tulip, T. H. J. Am. Chem. Soc. 1981, 103, 5984. (11) Isobe, K.; Andrews, D. G.; Mann, B. E.; Maitlis, P. M. J. Chem. Soc.,
- Chem. Commun. 1981, 809 (12) Röper, M.; Strutz, H.; Keim, W. J. Organomet. Chem. 1981, 219, C5.
- (13) Shaik, S.; Hoffmann, R.; Fisel, C. R.; Summerville, R. H. J. Am. Chem. Soc. 1980, 102, 4555.
- (14) Masters, C. Adv. Organomet. Chem. 1979, 17, 61.
 (15) Levisalles, J.; Francoise, R.-M.; Rudler, H. J. Chem. Soc., Chem. Commun. 1981. 152
- (16) Dimas, P. A.; Shapley, J. R. J. Organomet. Chem. 1982, 228, C12.
 (17) Triplett, K.; Curtis, M. D. J. Am. Chem. Soc. 1975, 97, 5747.
 (18) Cotton, F. A.; Walton, R. A. "Multiple bonds Between Metal Atoms";
- Wiley: New York, 1982.
- (19) Creswick, M.; Bernal, I.; Reiter, B.; Herrmann, W. A. Inorg. Chem. 1982. 21. 645
 - (20) Kostic, N. M.; Fenske, R. F. Inorg. Chem. 1983, 22, 666

(21) To date, seven distinct reaction pathways between Cp2Mo2(CO)4 and diazoalkanes have been observed, depending on the nature of the diazoalkane substituents. See ref 1c.



Figure 1. ORTEP drawing of $(\pi - C_5H_4Me)_2Mo_2(CO)_4(\mu - C_{13}H_8)$ (4').



Figure 2. Simplified MO diagram showing the effect of bonding a μ -CH, ligand along the -x axis (4a) and along the -y axis (3a). In this diagram, the $Cp_2Mo_2(CO)_4$ fragment is the same as shown in Figure 1.

reochemical restraint would prohibit complexation of the phenyl ring. Such indeed is the case, the reaction of 9-diazofluorene with 1 or its methylcyclopentadienyl analogue 1' proceeds at room temperature as shown in eq 3 to give 4 in 40-50% isolated yields.



There was no evidence for the presence of an intermediate diazo complex analgous to 2. Elemental and spectroscopic analyses were consistent with a symmetrically bridged structure as shown in eq 3.22

(22) Anal. Calcd. for 4': C, 55.61; H, 3.54. Found: C, 55.68; H, 3.43. ¹H NMR (360 MHz, C₆D₆, 25 °C) δ 1.18 (Me), 4.11 (A₂B₂, $\Delta\delta_{AB} = 112$ Hz, $J_{AB} = 2.4$ Hz, Cp), 7.2–8.0 (ABCD, Ar); ¹³C[¹H] (90.56 MHz, C₇D₈, 25°C) δ 236.1 (CO), 164.5 (μ -C).

⁺Dedicated to the memory of Rowland Pettit, 1927-1981.

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 3σ). 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 $Cp_2Mo_2(CO)_6$ (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 \pm 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 CH_2 model of 4. Although there is a formal Mo-Mo triple bond $(\sigma^2 \delta^2 \delta^{*2} \pi_{yz}^2 \pi_{xz}^2)$; (Figure 2) in the $Cp_2Mo_2(CO)_4$ 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 $Cp_2Mo_2(CO)_4$ fragment to 0.21 in $Cp_2Mo_2(CO)_4(\mu$ -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 CH_2 fragment in **3a** (Figure 2) is bonded along the -y axis, and it is the π_{y_2} and $\pi^*_{y_2}$ 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

- (27) Boileau, A. M.; Orpen, A. G.; Stansfield, R. F. D.; Woodward, P. J. Chem. Soc., Dalton Trans. 1982, 187 and references therein.
- (28) Chisholm, M. H.; Huffman, J. C.; Leonelli, J.; Rothwell, I. P. J. Am. Chem. Soc. 1982, 104, 7030.
- (29) Chisholm, M. H.; Huffman, J. C.; Rothwell, I. P. J. Am. Chem. Soc. 1981, 103, 4245 (30) Chisholm, M. H.; Corning, J. F.; Huffman, J. C. Inorg. Chem. 1982,
- 21, 286. (31) Rheingold, A. L.; Foley, M. J.; Sullivan, P. J. J. Am. Chem. Soc.
- 1982, 104, 4727. (32) Kamata, M.; Yoshida, T.; Otsuka, S.; Hirotsu, K.; Higuchi, T. J. Am. Chem. Soc. 1981, 103, 3572.
- (33) Endrich, K.; Korswagen, R.; Zahn, T.; Ziegler, M. L. Angew. Chem., Int. Ed. Engl. 1982, 21, 919
- (34) Solis, H. E.; Barcelo, I. D.; Curtis, M. D., unpublished results, 1983.

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.

Acknowledgment. We thank the National Science Foundation (CHE-8305235) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We also thank Drs. D. N. Duffy and L. Messerle for experimental assistance.

Registry No. 1 (R = C_5H_5), 56200-27-2; 1' (R = C_5H_4Me), 69140-73-4; 4, 85957-07-9; 4', 85957-08-0; 9-diazofluorene, 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

Y. Ohta,* S. Abe, H. Komura, and M. Kobayashi

Suntory Institute for Bioorganic Research Wakayamadai, Shimamoto-cho, Osaka 618, Japan Received February 4, 1983

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 radio-labeling 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

- (2) Fries, K. Beitr. Biol. Pflanz. 1964, 40, 177
- (3) Pryce, R. J. Phytochemistry 1971, 10, 2679-2685.

- (4) Gorham, J. Prog. Phytochem. 1914, 1017, 12017 (2017).
 (5) Abe, S.; Ohta, Y. Phytochemistry, in press.
 (6) Ohta, Y.; Katoh, K.; Miyake, K. Planta 1977, 136, 229-232.
 (7) Katoh, K.; Ishikawa, M.; Miyake, K.; Ohta, Y.; Hirose, Y.; Iwamura,
- T. Physiol. Plant. 1980, 49, 241-247.

⁽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 $I \ge 3\sigma(I)$

⁽²⁴⁾ Klinger, R. J.; Butler, W. M.; Curtis, M. D. J. Am. Chem. Soc. 1978, 100, 5034.

⁽²⁵⁾ Adams, R. D.; Collins, D. M.; Cotton, F. A. Inorg. Chem. 1974, 13, 1086.

⁽²⁶⁾ EHMO calculations were performed with R. Hoffmann's parameters and program ICON8: Kubáček, P.; Hoffmann, R.; Zoleněk, H. Organometallics 1982, 1, 180.

⁽¹⁾ Valio, I. F. M.; Burdon, R. S.; Schwabe, W. W. Nature (London) 1969, *223*, 1176–1178.