

## The Structure of Dimeric Azulenetricarbonylmethylmolybdenum, $[\text{C}_{10}\text{H}_8\text{Mo}(\text{CO})_3\text{CH}_3]_2$

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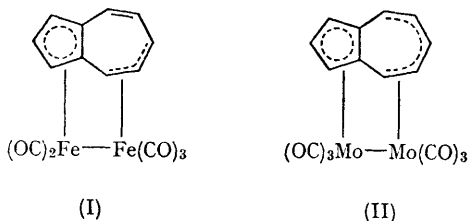
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WE have previously ascertained the nature of the azulene-metal bonding in azulenedi-iron pentacarbonyl<sup>1</sup> (I) and azulenedimolybdenum hexacarbonyl<sup>2</sup> (II).

These two molecules represent the only known azulene-metal carbonyl species in which two metal atoms are associated with a single azulene ligand. However, other complexes are known for which the

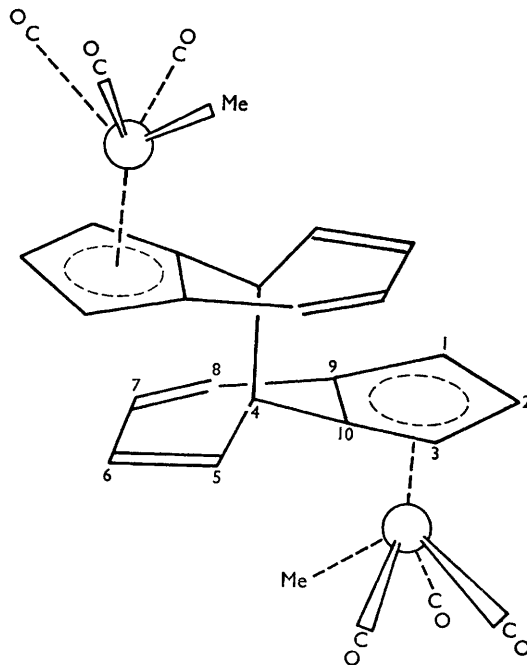
azulene : metal ratio is 1 : 1; *i.e.*,  $[\text{C}_{10}\text{H}_8\text{V}(\text{CO})_4]_2$ ,<sup>3</sup>  $[\text{C}_{10}\text{H}_8\text{Mn}(\text{CO})_3]_2$ ,<sup>4</sup> and  $[\text{C}_{10}\text{H}_8\text{Mo}(\text{CO})_3\text{Me}]_2$ .<sup>5</sup> A number of different formulations for these species have been suggested,<sup>4-6</sup> but King and Bisnette<sup>5</sup> have suggested that these molecules each contain a  $\pi$ -cyclopentadienyl-metal linkage and that dimerization occurs *via* a carbon-carbon bond between the seven-membered rings of the two

azulene systems. The preparative route to  $[\text{C}_{10}\text{H}_8\text{Mo}(\text{CO})_3\text{Me}]_2$  yields a single crystalline product and it appears that (in this case, at least) the stereochemistry of carbon-carbon coupling is specific. However, lack of resolution in the  $^1\text{H}$  n.m.r. spectrum of  $[\text{C}_{10}\text{H}_8\text{Mo}(\text{CO})_3\text{Me}]_2$  has excluded any unambiguous assignment of the stereochemistry of dimerization.<sup>5</sup>



We have therefore undertaken a single-crystal X-ray diffraction study of dimeric azulene-tricarbonylmethylmolybdenum to establish this point. The complex crystallizes in space group  $P\bar{1}$  (No. 2) with  $a = 10.00$ ,  $b = 8.36$ ,  $c = 8.19$  Å,  $\alpha = 107.3^\circ$ ,  $\beta = 89.3^\circ$ ,  $\gamma = 100.4^\circ$ ,  $Z = 1$ . The structure was solved by conventional Patterson, Fourier, and least-squares refinement techniques. Using complete data ( $\sin\theta_{\text{max}} = 0.38$ ; Mo- $K_\alpha$  radiation) collected with a Buerger Automated Diffractometer, the present discrepancy index is 5.83% for the 1438 observable reflections. All non-hydrogen atoms have been accurately located, present e.s.d.'s being  $\sim 0.013$  Å for Mo-C and  $\sim 0.018$  Å for C-C, bond lengths. Furthermore, each hydrogen atom associated with the azulene ligand has also been unambiguously located. (The hydrogen atoms associated with the methyl group have not been located, presumably due to rotation of the methyl group about the Mo-C axis.) The molecule possesses a crystallographic centre of symmetry, the two azulene ligands being bonded *via ortho-ortho* (i.e., 4,4') coupling (see Figure). The molybdenum atom lies 2.025 Å below the planar (r.m.s. deviation 0.008 Å)  $\pi$ -cyclopentadienyl ring. The Mo-C distances vary systematically around the five-membered ring, the greatest distance being that involving C-9, the atom immediately above the

methyl group [Mo-C-1 = 2.359, Mo-C-2 = 2.287, Mo-C-3 = 2.314, Mo-C-10 = 2.392, Mo-C-9 = 2.439 Å]. This "tilting" of the  $\pi$ -cyclopentadienyl ligand has been discussed before<sup>7</sup> and appears to be general for  $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{L}$  systems. The seven-membered ring is distinctly nonplanar, due mainly to the influence of the tetrahedral C-4. The deviations with respect to the least-squares plane of the five-membered ring are:  $\delta(\text{C-4}) = +0.141$ ,  $\delta(\text{C-5}) = -0.685$ ,  $\delta(\text{C-6}) = -0.750$ ,  $\delta(\text{C-7}) = -0.175$ ,  $\delta(\text{C-8}) = +0.129$  Å.



FIGURE

The mean Mo-CO bond-distance is 1.996 Å as compared to the Mo-CH<sub>3</sub> distance of 2.383 Å. Angles in the Mo(CO)<sub>3</sub>Me portion of the molecule are identical, within experimental error, with those observed in  $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{Et}$ <sup>8</sup> and  $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{C}_3\text{F}_7$ .<sup>7</sup>

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<sup>6</sup> M. A. Bennett, *Adv. Organometallic Chem.*, 1966, **4**, 366.

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<sup>8</sup> M. J. Bennett and R. Mason, *Proc. Chem. Soc.*, 1963, 273; M. J. Bennett, Ph.D. Thesis, Sheffield, 1965.