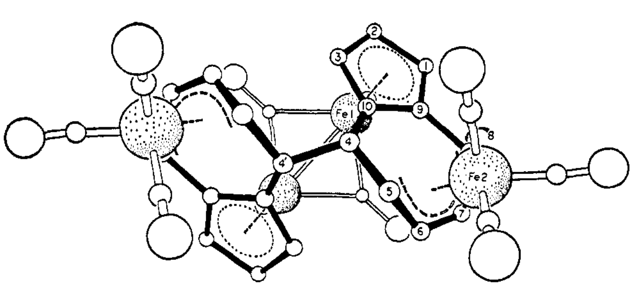
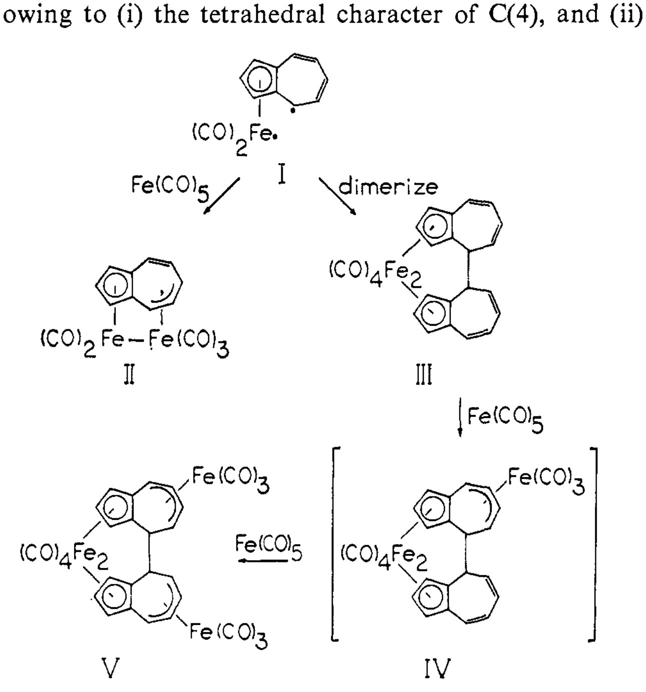


Figure 1. The $(C_{10}H_8)_2Fe_4(CO)_{10}$ molecule viewed down *b*. Note that terminal carbonyl groups lie almost immediately below Fe(1) and Fe(1′).

$C_3H_7)(CH_3)_2C_{10}H_5Mo_2(CO)_6$,[6,8] $C_{10}H_8Mn_2(CO)_6$,[9] $[C_{10}H_8Mo(CO)_3CH_3]_2$[10]}, the five-membered ring of the azulene nucleus behaves as a π-cyclopentadienyl ligand. Carbon–carbon distances within this planar (root-mean-square deviation = 0.017 Å) ring average 1.424 Å. Fe(1) lies 1.757 Å below this plane, with individual iron–carbon distances varying from 2.091 ± 0.008 to 2.191 ± 0.007 Å. Within the *seven-membered* ring, C(9) and C(10) are already engaged in the π-cyclopentadienyl–metal bond, C(4) is involved in the bond joining the two azulene nuclei, and the remaining four atoms [C(5) through C(8)] participate in a butadiene–$Fe(CO)_3$ linkage in which Fe–C(terminal) and Fe–C(central) distances average 2.131 ± 0.008 and 2.038 ± 0.008 Å, respectively. Bond lengths around the coordinated butadiene system (1.435 ± 0.011, 1.364 ± 0.011, 1.434 ± 0.011 Å) are in good agreement with those obtained from other molecules.[11,12]

The azulene ligand is severely distorted from planarity owing to (i) the tetrahedral character of C(4), and (ii) the usual[11,12] "bend" across the ends of the butadiene system. The formation of a 4-*endo*-4′-*endo*-diazulene system leads to some short intramolecular contacts and to strain within the molecule, which may be exemplified by the significant variation ($\Delta/\sigma \sim 14$) in Fe–C distances around the π-cyclopentadienyl system and (possibly) by the rather long C(4)–C(4′) bond length of 1.583 ± 0.014 Å.



The final elucidation of the stoichiometry and molecular configuration of $(C_{10}H_8)_2Fe_4(CO)_{10}$ leads to a systematization of azulene–iron carbonyl chemistry and helps to extend the previously recognized[10b] pattern of azulene–metal carbonyl reactions. The known compounds $C_{10}H_8Fe_2(CO)_5$ (II),[5] $[C_{10}H_8Fe(CO)_2]_2$ (III),[13] and $(C_{10}H_8)_2Fe_4(CO)_{10}$ (V) [and the presently unknown $(C_{10}H_8)_2Fe_3(CO)_7$ (IV)] may be seen to be derived from the postulated[10b] intermediate (I).

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Formation and Structure of a σ-Aryl Derivative of Molybdenum, π-$C_7H_7Mo(CO)_2C_6F_5$

Sir:

A recent joint program in our laboratories has been concerned with comparisons of the relative stabilities and molecular structures of organotransition metal compounds containing σ-bonded organic ligands.[1] Studies in the σ-arylmolybdenum series would seem especially rewarding, since corresponding σ-alkyl, σ-perfluoroalkyl, and σ-acyl analogs have recently been examined in appreciable detail.[2] Unfortunately, well-characterized σ-aryl derivatives of molybdenum were hitherto unknown, various attempts at preparing them having met with failure.[3,4] We now report the first example of an organomolybdenum compound containing a σ-aryl ligand and describe the results of a single-crystal X-ray crystallographic investigation which confirm the structure of the new compound and provide direct evidence for metal–carbon multiple bonding in this transition-metal aryl.

Treatment of pentafluorophenylmagnesium bromide in tetrahydrofuran solution[5] with an equimolar amount of π-cycloheptatrienyldicarbonylmolybdenum iodide,[6]

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(4) A patent reference [J. W. Culmer, U. S. Patent 2,843,547 (1958); *Chem. Abstr.*, **52**, 21047 (1958)] claims that a vigorous reaction between C_6H_5MgBr and $MoCl_3$ in ethyl ether, followed by hydrolysis, precipitates "solid $(C_6H_5)_3Mo$," although further details are not given.

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followed by column chromatography on Florisil under nitrogen and subsequent recrystallization from methylene chloride–hexane, has produced π-cycloheptatrienyldicarbonylmolybdenum σ-pentafluorophenyl, π-$C_7H_7Mo(CO)_2C_6F_5$, in *ca.* 55% yield.[7,8] The product was isolated in the form of dichroic (green–red), air-stable crystals of mp 209° dec. *Anal.* Calcd for $C_{15}H_7F_5MoO_2$: C, 43.92; H, 1.72; F, 23.16; Mo, 23.39. Found: C, 43.49; H, 1.88; F, 22.71; Mo, 22.66. The infrared spectrum (KBr) exhibited two strong terminal carbonyl stretching bands at 1995 and 1960 cm^{-1}, as well as absorptions near 1500 cm^{-1} and between 1050 and 950 cm^{-1} which are characteristic[9] of a pentafluorophenyl group. The proton nmr spectrum of the new compound consisted of a single sharp peak at τ 4.25, assignable to the protons of the π-C_7H_7 group.

The complex crystallizes in the centrosymmetric orthorhombic space group Pnma (D_{2h}^{16}; no. 62) with a = 7.57 Å, b = 13.22 Å, c = 14.23 Å, V = 1424 Å^3, Z = 4. Observed and calculated densities are respectively 1.78 ± 0.04 and 1.75 g cm^{-3}. A set of X-ray diffraction data complete to $\sin\theta = 0.40$ (Mo Kα radiation) was collected on a 0.01° incrementing Buerger automated diffractometer using a "stationary-background, ω-scan, stationary-background" counting sequence. A combination of Patterson, Fourier, and least-squares refinement techniques has resulted in the location of all atoms including hydrogens, the present discrepancy index being R_F = 5.9% for the 1269 independent nonzero reflections.

The molecule possesses an exact, *i.e.*, crystallographically required, mirror plane (see Figure 1). Within the limits of experimental error, the π-cycloheptatrienyl ligand has the anticipated D_{7h} symmetry; individual carbon–carbon bond lengths vary from 1.374 ± 0.014 to 1.462 ± 0.013 Å (averaging 1.409 Å), and the root-mean-square deviation from planarity is 0.016 Å. The molybdenum atom lies 1.661 Å below the seven-membered ring, with molybdenum–carbon distances ranging from 2.303 ± 0.009 to 2.334 ± 0.009 Å (av 2.318 Å). [A survey of π-cyclopentadienylmolybdenum species[2] shows that Mo–C(π-cyclopentadienyl) distances average ~2.35 Å, and the mean perpendicular metal→plane-of-ring distance is ~2.00 Å. A comparison of these figures with the values obtained from the present structural analysis (*vide supra*) provides further evidence[10] that constancy of the metal–C(arene) distance, rather than constancy of the perpendicular metal→plane-of-ring distance, is the dominant feature in transition metal arenes as the size of the cyclic ligand varies.]

The molybdenum pentafluorophenyl bond length of 2.244 ± 0.009 Å is some 0.14 Å (*i.e.*, ~15σ) shorter than the accepted molybdenum–alkyl bond length of 2.38 Å.[2b] After allowing for the difference in covalent radii of sp^2- and sp^3-hybridized carbon atoms, it is seen that the present Mo–C_6F_5 distance is contracted ~0.11 Å (12σ) relative to a Mo–C(sp^2) linkage of unit bond order. We feel, therefore, that this diffraction study provides the first unequivocal evidence for multiple-bond character in a metal–aryl linkage. A further interesting feature is that the internal angle at C_1 is 114.1 ± 0.8°, *i.e.* more than 7σ below the ideal sp^2 value. This phenomenon is common to all metal aryls that have been studied. Corresponding angles are 112.1 ± 1.0° in $[P(C_2H_5)_2C_6H_5]_2Co(mesityl)_2$,[11] 114.0 ± 0.9° in $(THF)_3Cr[p\text{-tolyl}]Cl_2$ (THF = tetrahydrofuran),[12] 114.2 ± 1.3° in $(\pi\text{-}C_5H_5)Ni[P(C_6H_5)_3]C_6F_5$,[1,13] and 115.9 ± 0.7° in $(\pi\text{-}C_5H_5)Ni[P(C_6H_5)_3]C_6H_5$.[1,13] Finally, it should be noted that all previously reported metal–aryl distances [*viz.* Co^{II}–mesityl = 1.961 ± 0.012 Å,[11] Cr^{III}-p-tolyl = 2.014 ± 0.010 Å,[12] Ni^{II}–C_6H_5 = 1.919 ± 0.013 Å,[1] Ni^{II}–C_6F_5 = 1.914 ± 0.014 Å,[1] Rh^{IV}–C_6H_5 = 2.05 Å[14]] are likely to be significantly shorter than the analogous metal-*alkyl* distances.

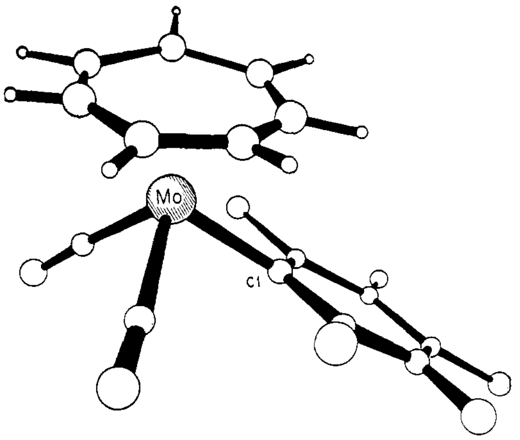

Figure 1. The π-$C_7H_7Mo(CO)_2(\sigma\text{-}C_6F_5)$ molecule. Important dimensions not in the text include Mo–CO = 2.017 ± 0.010 Å and C–O = 1.131 ± 0.012 Å.

Studies on these and related systems are continuing and will be reported at a later date.

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(7) The product is also apparently the first reported example in which a π-C_7H_7 ligand provides stabilization, at least in part, to a σ-bonded organic ligand on the same transition metal. For a discussion of other examples of such stabilization, see M. D. Rausch, Advances in Chemistry Series, No. 62, American Chemical Society, Washington, D. C., 1966, p 486.

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