alcohol 10 gives 10% ketone 11, resulting from cyclopentyl migration, and 90% ketone 12, from cyclopropyl migration.[7]

The Baeyer-Villiger case is a mechanistic extreme in which the high electronegativity of the migration terminus (oxygen) and the exceptional strength of the $C=O$ π bond thrust an inordinately large share of positive charge upon the migrating group M, i.e., the resonance structure 13 is a large contributor to the transition state.[8,9] This factor dominates the rearrangement of 9[6] and that of the corresponding Baeyer-Villiger intermediates in other model systems,[10] all of which show cyclopropyl to be a poor migrating group relative

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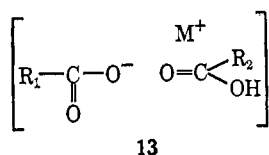
to other sec-alkyl groups. Presumably because the high s character of the migrating ring carbon in cyclopropyl makes it rather electronegative, the relative contribution of resonance structure 13 is diminished and hence the transition state is destabilized. When the migration terminus is carbon, as in cases 1 and 10, the positive charge resides to a smaller extent on the migrating group, and cyclopropyl migration becomes relatively more important than in 9. What is at first surprising is the net preference for migration of the less efficient migrating group (cyclopropyl) to give the less stable ring-expanded cation 6, which only an appended hydride shift finally converts to the more stable cation 2. The mechanism is curiously indirect, since 2 in principle could be generated in one step from 1 by migration of the better migrating group (cyclopentyl). This behavior seems to be largely a result of steric inhibition of cyclopropylcarbinyl resonance.[11] Although the fully developed cyclopropylcarbinyl cation 2 has the favorable "bisected" geometry,[12] the transition state 14[13] for direct cyclopentyl migration leading to 2 does not. With the ordinary conjugative interaction thus damped,
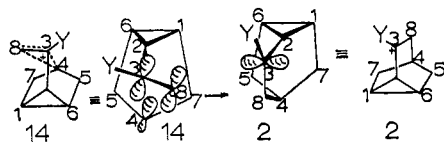
the cyclopropane ring is less efficient than a simple alkyl group as a stabilizer of adjacent positive charge.[11] When there is an additional contiguous source of electron supply to the migration origin (for example, the OH

(7) J. T. Lumb and G. H. Whitham, Tetrahedron, 21, 499 (1965).

(8) P. Magee, Ph.D. Dissertation, University of California at Los Angeles, 1955; S. Winstein and P. Magee, unpublished work.

(9) (a) J. A. Berson and S. Suzuki, J. Am. Chem. Soc., 81, 4088 (1959); (b) for a review, see P. A. S. Smith in "Molecular Rearrangements," Vol. I, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, pp 577-591.

(10) R. R. Sauers and R. W. Uebersax, J. Org. Chem., 30, 3939 (1965).

(11) For another example, see H. C. Brown and J. D. Cleveland, J. Am. Chem. Soc., 88, 2051 (1966).

(12) See references cited in ref 4 and 11.

(13) Positions in 2 are designated to give its carbon atoms the same numbers as their counterparts in 14.

group in 10), the effect is mitigated, and some cyclopentyl migration occurs.

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The Characterization and Molecular Configuration of Diazulenetetrairon Decacarbonyl

Sir:

We have recently shown that the complex $(CH_3)_3C_{10}H_5Ru_4(CO)_9$ has a 4,6,8-trimethylazulene ligand bonded to three atoms of a tetrahedral ruthenium cluster.[1] This unexpected result has prompted our examination of a polynuclear azulene-iron carbonyl complex which previously had been tentatively formulated[2] as "$(C_{10}H_8)_2Fe_5(CO)_{13}$." We now report that this species should be reformulated as $(C_{10}H_8)_2Fe_4(CO)_{10}$, that it does not contain a cluster of four metal atoms, but that it does show some features novel to azulene-metal carbonyl chemistry.

The complex was prepared by the method of Burton, et al.[2] Beautiful multifaceted deep-brown crystals of stoichiometry $(C_{10}H_8)_2Fe_4(CO)_{10} \cdot C_2H_4Cl_2$[3] were obtained by slow cooling of a solution in 1,2-dichloroethane-hexane. The compound crystallizes in the centrosymmetric monoclinic spacegroup C2/c (C_{2h}^6; no. 15) with $a = 17.296$ Å, $b = 15.541$ Å, $c = 12.915$ Å, $\beta = 114.53°$, $Z = 4$. Observed and calculated densities are 1.82 ± 0.02 and 1.805 g cm^{-3}. A set of X-ray diffraction data complete to sin $\theta = 0.40$ (Mo Kα radiation) were collected with a 0.01° incrementing Buerger automated diffractometer, using a "stationary-background, ω-scan, stationary-background" counting sequence. The structure was solved by Patterson, Fourier, and least-squares refinement techniques, the discrepancy index at the present stage of refinement being $R_F = 6.61$% for 2040 independent nonzero reflections. Refinement is continuing.

The $(C_{10}H_8)_2Fe_4(CO)_{10}$ molecule has exact (i.e., crystallographically required) C_2 symmetry (see Figure 1) and is derived from two trans-$C_{10}H_8Fe_2(CO)_5$ units which are linked both by a 4-endo-4'-endo carbon-carbon bond and by an Fe$_2$(CO)$_4$ bridge analogous to that found in $[\pi$-C$_5$H$_5$Fe(CO)$_2]_2$,[4] the Fe-Fe distance being 2.519 ± 0.002 Å. (However, the site symmetry of the Fe$_2$(CO)$_4$ moiety is C_2 in the present complex as opposed to C_i in the parent molecule.[4] Thus the Fe$_2$(CO)$_4$ fragment in $[\pi$-C$_5$H$_5$Fe(CO)$_2]_2$ is more-or-less planar, whereas there is an angle of 154.8° between the planes of the two carbonyl bridges in the $(C_{10}H_8)_2Fe_4(CO)_{10}$ molecule.) As in previously examined azulene complexes $\{C_{10}H_8Fe_2(CO)_5,$[5] $C_{10}H_8Mo_2(CO)_6,$[6,7] (i-

(1) M. R. Churchill and P. H. Bird, J. Amer. Chem. Soc., 90, 800 (1968).

(2) R. Burton, L. Pratt, and G. Wilkinson, J. Chem. Soc., 4290 (1960).

(3) (a) Mass spectroscopy showed the parent-iron peak at m/e 760. The accidental mass relationship ^{56}Fe = 2(^{12}C^{16}O) precluded an unequivocal structural assignment, but led to the partial formula $(C_{10}H_8)_2Fe_n(CO)_{18-2n}$. (b) The dichloroethane molecule is present only as solvent of crystallization.

(4) O. S. Mills, Acta Cryst., 11, 520 (1958).

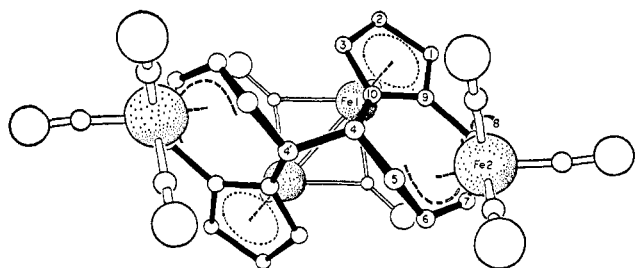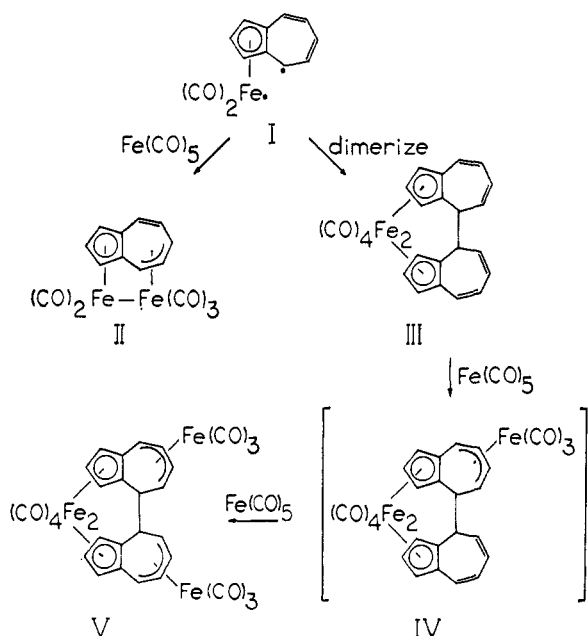(5) M. R. Churchill, Chem. Commun., 450 (1966); Inorg. Chem., 6, 190 (1967).

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').

$C_3H_7)(CH_3)_2C_{10}H_5Mo_2(CO)_8$,[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).

(13) R. B. King, *J. Amer. Chem. Soc.*, **88**, 2075 (1966).

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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]

(1) M. R. Churchill, T. A. O'Brien, M. D. Rausch, and Y. F. Chang, *Chem. Commun.*, 992 (1967).
(2) (a) M. R. Churchill and J. P. Fennessey, *Inorg. Chem.*, **6**, 1213 (1967); (b) P. H. Bird and M. R. Churchill, *ibid.*, **7**, 349 (1968); (c) M. R. Churchill and J. P. Fennessey, *ibid.*, **7**, 953 (1968). See also earlier studies cited in these references.
(3) T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **3**, 104 (1956); R. B. King and M. B. Bisnette, *J. Organometal. Chem.* (Amsterdam), **2**, 15, 38 (1964).
(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.
(5) C. Tamborski, E. J. Soloski, and J. P. Ward, *J. Org. Chem.*, **31**, 4230 (1966).
(6) R. B. King, "Organometallic Syntheses," Vol. 1, Academic Press Inc., New York, N. Y., 1965, p 141.

(6) M. R. Churchill and P. H. Bird, *Chem. Commun.*, 746 (1967).
(7) J. S. McKechnie and I. C. Paul, *ibid.*, 747 (1967).
(8) M. R. Churchill and P. H. Bird, *Inorg. Chem.*, in press.
(9) P. H. Bird and M. R. Churchill, *Chem. Commun.*, 145 (1968).
(10) (a) P. H. Bird and M. R. Churchill, *ibid.*, 705 (1967); (b) *Inorg. Chem.*, **7**, 349 (1968).
(11) M. R. Churchill and R. Mason, *Proc. Roy. Soc.* (London), A301, 433 (1967).
(12) M. R. Churchill and R. Mason, *Advan. Organometal Chem.*, **5**, 93 (1967).