These observations lead us to hypothesize an extension of the earlier[1,2] rationalization: at high alkane concentrations H abstraction by free and π-complexed chlorine atom occurs; at low concentrations of alkane a σ complex is generated that acts as the third H-abstracting species. The proposed σ-complex is the cyclohexadienyl radical (**1**), which reacts as shown in Scheme I.

There seems to be no firm published data for the rate of addition of chlorine to benzene. Preliminary results obtained in our laboratory[3] from photoinitiated chlorine additions to tetrachloroethene[4] and benzene suggest that a rate constant of 1.3×10^9 L mol^{-1} s^{-1} applies to the loss of benzene, presumed to lead ultimately to $C_6H_6Cl_6$. Thus, the increase of selectivity at low alkane concentrations, indicative of the appearance of the third H abstractor, is similar to the rate of chlorination of benzene.

Nonetheless, the major product is alkyl chloride when alkane is present. A reaction run in 8 M benzene, with 0.1 M 2,4-dimethylpentane and 0.01 M Cl_2, produces a mixture of 1°, 2°, and 3° alkyl chlorides in 85% yield, based on Cl_2.[5]

We are examining a broad range of interactions of chlorine atoms to learn under what circumstances other selective chlorinating agents may be generated.

Registry No. $(CH_3)_2CHCH(CH_3)_2$, 79-29-8; Cl, 22537-15-1.

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On the Stability of Early-Transition-Metal Metallacyclobutadiene Complexes

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Several years ago Katz proposed that the mechanism of the acetylene metathesis reaction parallels that of the olefin metathesis reaction by proceeding through a metallacyclobutadiene intermediate, presumably involving a metal–carbyne complex.[1] This proposal received strong support from Schrock's observation that certain tungsten(VI) alkylidyne complexes are effective acetylene metathesis catalysts.[2] More recently, Schrock, Churchill, and co-workers have isolated and structurally characterized the product resulting from the addition of 1 equiv of 2-butyne to the alkylidyne complex W(C-*t*-Bu)(dme)Cl_3 and have found it to be the tungstenacyclobutadiene complex W(C-*t*-Bu)(MeC≡CMe)Cl_3, in which there is an essentially planar WC_3 ring.[3]

The existence of stable metallacyclobutadiene complexes raises several interesting questions. Foremost among these is why such systems should be stable whereas the organic analogue cyclobutadiene is only transiently so. Secondly, the geometry of the WC_3 ring[3] is somewhat surprising in that the C_α–C_β–C_α angle is quite large (118.9 (8)°) and the W–C_β bond length is quite short (2.115 (8) Å). Finally, the stability of metallacyclobutadiene complexes is undesirable if early-transition-metal alkylidyne complexes are to be effective catalysts, and it is of interest to determine what might be done to destabilize them. To these ends, Fenske–Hall molecular orbital calculations[4] have been performed on the model compound $Cl_3WC_3H_3$ and its metallacyclobutadienoid core $[WC_3H_3]^{3+}$.[5]

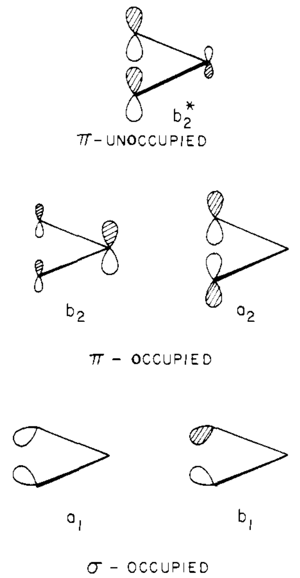

Figure 1. Frontier orbitals of $[C_3H_3]^{3-}$. The hydrogen atoms are not pictured.

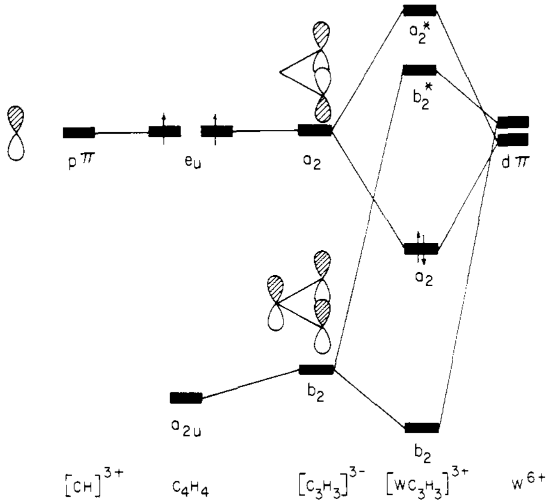

Figure 2. Qualitative MO diagram showing the differences between the interaction of the b_2 and a_2 orbitals of $[C_3H_3]^{3-}$ with the pπ orbital of $[CH]^{3+}$, to form C_4H_4, and the dπ orbitals of W^{6+}, to form $[WC_3H_3]^{3+}$.

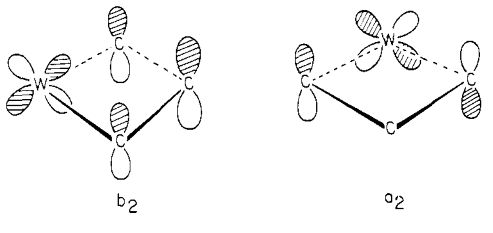

Figure 3. Orbital interactions in the b_2 and a_2 bonding orbitals of $[WC_3H_3]^{3+}$.

The comparison of bonding in C_4H_4 and $[W(C_3H_3)]^{3+}$ is best facilitated by contrasting the interactions of the "p^0" fragment $[CH]^{3+}$ and the d^0 ion W^{6+} with a $[C_3H_3]^{3-}$ fragment, which may be considered a doubly deprotonated allyl ion. The frontier orbitals of $[C_3H_3]^{3-}$ are shown in Figure 1. The two σ lone-pair orbitals, a_1 and b_1, are occupied and will form σ bonds to either $[CH]^{3+}$

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(1) Katz, T. J.; McGinnis, J. *J. Am. Chem. Soc.* **1975**, *97*, 1592.

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(3) Pederson, S. F.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *J. Am. Chem. Soc.* **1982**, *104*, 6808.

(4) Hall, M. B.; Fenske, R. F. *Inorg. Chem.* **1972**, *11*, 768.

(5) Calculational details: The bond lengths and angles are from ref 3 except for C–H bond lengths, which were assumed to be 1.08 Å. The H–C–W angle was chosen such that the C–H vector bisects the W–C–C angle. The geometry was idealized to C_{2v} symmetry. Basis functions were derived by using the method of ref 6.

(6) Bursten, B. E.; Jensen, J. R.; Fenske, R. F. *J. Chem. Phys.* **1978**, *68*, 3320.

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or W^{6+} by direct donation into empty orbitals of the appropriate symmetry. The σ bonding is analogous to that in metallacyclobutanes[7] and will not be discussed further here. There are three π frontier orbitals in $[C_3H_3]^{3-}$, b_2 (bonding), a_2 (nonbonding), and b_2^* (antibonding), of which the first two are occupied. The b_2^* orbital, being very high in energy, does not contribute significantly to any occupied orbitals of $[WC_3H_3]^{3+}$ and may be ignored henceforth. The π interaction will be between the b_2 and a_2 orbitals of $[C_3H_3]^{3-}$ and the available π orbitals on either $[CH]^{3+}$ or W^{6+}; it is the difference in the latter that accounts for the differences between the organic and organometallic systems, as shown qualitatively in Figure 2. In $[CH]^{3+}$ there is one pπ orbital available, and its interaction with the π orbitals of $[C_3H_3]^{3-}$ leads to the familiar orbital pattern for C_4H_4, in which the HOMO is a half-filled nonbonding e_u orbital (under D_{4h} symmetry). In contrast to the situation in $[CH]^{3+}$, there are two dπ orbitals in a d^0 metal ion that can interact with the b_2 and a_2 orbitals of $[C_3H_3]^{3-}$. The principle bonding interactions, shown in Figure 3, consist of stabilization of *both* the b_2 and a_2 orbitals of $[C_3H_3]^{3-}$, with concomitant formation of b_2^* and a_2^* antibonding orbitals.

It is apparent that the major difference between the bonding in C_4H_4 and $[WC_3H_3]^{3+}$ is in the HOMO of each. In square C_4H_4, the π orbital of $[CH]^{3+}$ cannot interact with the a_2 orbital of $[C_3H_3]^{3-}$, necessarily leading to the nonbonding HOMO which is characteristic of antiaromatic systems. In $[WC_3H_3]^{3+}$, by contrast, the interaction of one of the dπ orbitals with the a_2 orbital of $[C_3H_3]^{3-}$ produces a strongly bonding orbital in which the W is π bonded to the α-carbons (Figure 3). This type of interaction has been anticipated by Thorn and Hoffmann.[8] Mulliken population analysis of the a_2 orbital of $[WC_3H_3]^{3+}$ indicates that it consists of nearly equal contributions from the W dπ (52%) and the $[C_3H_3]^{3-}$ a_2 (48%) orbitals, and the overlap population between the two (0.350) is sizable. The LUMO of $[WC_3H_3]^{3+}$ is 5.0 eV above the a_2 HOMO, again indicative of the strong stabilization within the a_2 orbital. A fully occupied, strongly π-bonding HOMO in a cyclic system is characteristic of aromatic systems, and despite its being a four-π-electron system, it is tempting to call $[WC_3H_3]^{3+}$ a metalloaromatic system; this concept was first used to rationalize the stability of cyclobutadiene–metal complexes vis-à-vis the instability of cyclobutadiene.[9] As is the case in $(C_4H_4)Fe(CO)_3$, the greater flexibility of d orbitals allows favorable bonding interactions in $[WC_3H_3]^{3+}$ not achievable in the purely organic system C_4H_4. It is also of interest to note that the HOMO stabilization evident in metallacyclobutadiene complexes is not possible in dimetallacyclobutadiene complexes wherein there are no C–C nonbonding orbitals to stabilize.[10]

The analysis of $[WC_3H_3]^{3+}$ also accounts for the anomalously short W–C_β distance in the tungstenacyclobutadiene system.[3] The b_2 orbital of $[C_3H_3]^{3-}$, which has its largest contribution (48%) from the β-carbon, interacts strongly with the dπ orbital which is spatially directed toward it (Figure 3). This results in the b_2 orbital of $[WC_3H_3]^{3+}$ having an 18% contribution from the W dπ orbital. Thus, the β-carbon is pulled toward the W center by an across-the-ring interaction. The MO calculation of $Cl_3WC_3H_3$[11] indicates that the LUMO of the complex, which is 4.2 eV above the HOMO, is essentially the b_2^* orbital of $[WC_3H_3]^{3+}$, i.e., the antibonding counterpart of the across-the-ring bond. It is expected, therefore, that a d^1 or d^2 metallacyclobutadiene complex would have an appreciably reduced interaction between the metal center and the β-carbon relative to the d^0 system; it is noted that two late-transition-metal adducts of the triphenylcyclopropenium cation,[12] while possessing metallacyclobutadienoid cores, do not exhibit unusually short M–C_β bonds. Since the M–C_β interaction helps to stabilize the d^0 metallacyclobutadiene, an undesirable situation if it is the catalytic intermediate in acetylene metathesis, it may be the case that d^1 or d^2 systems will be better catalysts than the d^0 ones.

Acknowledgment. Thanks are due to Professors R. R. Schrock and M. R. Churchill for a preprint of ref 3.

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[8] Thorn, D. L.; Hoffmann, R. *Nouv. J. Chim.* **1979**, *3*, 39.

[9] Bursten, B. E.; Fenske, R. F. *Inorg. Chem.* **1979**, *18*, 1760.

[10] Hoffman, D. M.; Hoffmann, R.; Fisel, C. R. *J. Am. Chem. Soc.* **1982**, *104*, 3858.

[11] The detailed MO description of $Cl_3WC_3H_3$, as well as its metallatetrahedranoidal isomer, will be the subject of a subsequent publication.

[12] (a) $Cl(CO)(PMe_3)_2IrC_3Ph_3$: Tuggle, R. M.; Weaver, D. L. *Inorg. Chem.* **1972**, *11*, 2237. (b) $Cl_2(PMe_2Ph)_2RhC_3Ph_3$: Frisch, P. D.; Khare, G. P. *Ibid.* **1979**, *18*, 781.

Pentalenene Biosynthesis and the Enzymatic Cyclization of Farnesyl Pyrophosphate

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The recognition that farnesyl pyrophosphate (**1**, Scheme I) can serve as a biosynthetic precursor of all cyclic sesquiterpenes, of which nearly 200 individual skeletal types are now known, remains one of the outstanding theoretical triumphs of modern bioorganic chemistry.[2] Until recently, however, few examples had been reported of direct investigations of the key cyclization reactions, the bulk of the experimental evidence for the role of farnesyl pyrophosphate having rested on inference from the results of traditional early-precursor–late-product incorporation experiments.[3] Only in recent years, as attention has turned increasingly to the development of cell-free systems from plants and microorganisms, has it become possible to investigate directly the important and fascinating cyclases that lie at the heart of terpenoid biosynthesis.[4] We report below the preparation of a cell-free extract of *Streptomyces* that catalyzes the cyclization of *trans,trans*-farnesyl pyrophosphate to pentalenene (**2**),[5] the parent hydrocarbon[6] of the pentalenolactone family of sesquiterpene antibiotics.[8]

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[1] (a) Fellow of the Alfred P. Sloan Foundation, 1978–1982; National Institutes of Health Research Career Development Award, 1978–1983. (b) This work was supported by a grant from the National Institutes of Health, GM22172.

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[3] Cane, D. E. In "Biosynthesis of Isoprenoid Compounds"; Porter, J. W., Spurgeon, S. L., Eds.; Wiley: New York, 1981; pp 283–374.

[4] For additional examples of farnesyl pyrophosphate cyclases, see the following. (a) Bisabolene synthetase: Anastasis, P.; Freer, I.; Gilmore, C.; Mackie, H.; Overton, K.; Swanson, S. *J. Chem. Soc., Chem. Commun.* **1982**, 268. Overton, K. H.; Picken, D. J. *Ibid.* **1976**, 105. (b) Trichodiene synthetase: Evans, R.; Hanson, J. R. *J. Chem. Soc., Perkin Trans. 1* **1976**, 326. Cane, D. E.; Swanson, S.; Murthy, P. P. N. *J. Am. Chem. Soc.* **1981**, *103*, 2136. (c) See also for farnesyl pyrophosphate isomerase: Cane, D. E.; Iyengar, R.; Shiao, M.-S. *Ibid.* **1981**, *103*, 914. (d) For a comprehensive review of closely related geranyl pyrophosphate cyclases, see: Croteau, R. In ref 3, pp 225–282.

[5] Isolation: (a) Seto, H.; Yonehara, H. *J. Antibiot.* **1980**, *33*, 92. Synthesis: (b) Ohfune, Y.; Shirahama, H.; Matsumoto, T. *Tetrahedron Lett.* **1976**, 2869. (c) Annis, G. D.; Paquette, L. A. *J. Am. Chem. Soc.* **1982**, *104*, 4504.

[6] The role of pentalenene as a precursor of the more oxidized pentalenanes has been established by feeding experiments with intact cells. The requisite [1,13-^{3}H]pentalenene (**2**; 8.9 × 10^9 dpm/mmol) was prepared according to ref 5b by the use of ^3H-$NaBH_4$ to reduce the mercuric nitrate cyclization product of humulene (**6**). Oxidation of a portion of this labeled pentalenene to the corresponding 13-carboxylic acid methyl ester (**8**) established that 14% of the tritium label was at C-1 (1.3 × 10^9 dpm/mmol). Feeding of 7.1 × 10^8 dpm of [1,13-^{3}H]pentalenene to a culture of *Streptomyces* UC5319 gave labeled pentalenolactone (**9**; 0.7% incorporation, 6 × 10^7 dpm/mmol), pentalenolactone E (**10**; 0.2%, 1.7 × 10^7 dpm/mmol), pentalenolactone F (**11**;[7] 0.2%, 1.7 × 10^7 dpm/mmol), and pentalenic acid (**12**; 0.1%, 1.2 × 10^7 dpm/mmol), each isolated and rigorously purified as the derived methyl ester. The site of labeling was unambiguously confirmed by PCC oxidation of **12** to the corresponding ketone (**13**), which retained $\leq$1% of the original tritium activity (Scheme III).

[7] Tillman, A. M.; Cane, D. E., submitted for publication.

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