between the cyclopropenylium cation (3.0β) and the allyl cation (1.4β; approximated by **3**).

The results of this study are remarkable in that they suggest that highly sophisticated theoretical techniques are required to satisfactorily address problems pertaining to homoaromatic character.

π Complexing of Chlorine Atoms: Is That All There Is?

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Russell[1] and Walling and Mayahi[2] described the effect of solvation on the selectivity of chlorine atoms in hydrogen abstraction reactions. Aromatic solvents and carbon disulfide were found to be especially effective in moderating the H-abstracting reactions of chlorine atoms. This effect was rationalized with the concept of π complexation of the chlorine atom. While this rationalization was sufficient to explain most of the observations, there were some aspects that were not so felicitously consistent, and this led us to an exploration of an experimental region not encompassed in the original work.

The earlier studies used substrates at high concentrations, typically 1–3 M. With low concentration of substrates the H-abstracting species would live longer before encountering a substrate molecule. The π-complex rationalization would predict no change in selectivity with decreasing concentration of substrate, only, perhaps, a decrease in yield of chlorinated substrate. We report here that *a very marked increase of selectivity occurs with progressive diminution of the substrate concentration.*

The experimental design was essentially the same as in the earlier reports. Dilute Cl_2 in argon was bubbled through the deoxygenated reaction solutions while irradiating with a tungsten lamp. Conversions of substrate were kept low by limiting the amount of Cl_2 to preclude polychlorination, typically 5–15% conversions of alkane substrate. The substrate was 2,3-dimethylbutane, and the yields of primary and tertiary halides were determined by gas chromatography. We report here the tertiary to primary ratio on a per hydrogen basis (S).

Table I gives S as a function of alkane concentration in 4.0 M benzene solvent. At the highest concentrations of alkane these results are similar to those in the earlier reports; at low concentrations the selectivities are much higher. Since there is no change in the benzene concentration in this series of experiments, the π-complexation equilibrium cannot be affected.

$$\text{Cl}\cdot + \text{arene} \rightleftharpoons (\text{arene}\cdot\text{Cl})$$

All indications point to rapid establishment of equilibrium between free chlorine atom and the π complex—particularly in media where the arene is the solvent. Alteration of alkane concentration should not affect selectivity if the above species are the only two abstractors. The only effect of a 100-fold reduction of alkane concentration would be a corresponding increase in the average time required for an encounter between a chlorine atom and an alkane molecule: with 1 M alkane, $\sim 10^{-10}$ s, with 0.01 M alkane, $\sim 10^{-8}$ s. However, within this time frame, provided by using low alkane concentrations, it is apparent that the concentration of a more selective H abstractor is increasing.

Table I. Photochlorination of 2,3-Dimethylbutane in 4 M Benzene at 20 °C (CCl_3F as Diluent)

$[(CH_3)_2CHCH(CH_3)_2]^a$	$S(3°/1°)$
4.7	16.1
1.0	33.2
0.51	37.5
0.20	50.2
0.10	52.8
0.050	53.6
0.020	56.0

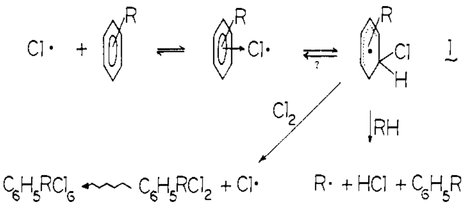
[a] mol L^{-1}.

Table II. Photochlorination of 2,3-Dimethylbutane in 4.0 M Carbon Disulfide at 13 °C (CCl_3F as Diluent)

$[(CH_3)_2CHCH(CH_3)_2]^a$	S (3°/1°)
5.8	22
2.0	34
1.0	51
0.51	60
0.25	73
0.11	93
0.051	107

[a] Mol L^{-1}.

Scheme I



Analogous occurrences have been observed in 4.0 M CS_2 in CCl_3F (Table II). In CCl_3F, as reported earlier,[1,2] there is no solvent effect: at all concentrations of alkane we find the tertiary to primary selectivity to be 4.15 ± 0.1, characteristic of a free chlorine atom chain.

The effect of Cl_2 concentration was examined by carrying out two sets of experiments in chlorobenzene. In the first set, the 2,3-dimethylbutane concentration was 2.0 M, and all conditions, except for the manner of Cl_2 introduction, were identical. In one experiment, chlorine was introduced over a 20-min period with steady illumination as described above. Under these conditions the color of chlorine was not evident, indicating a Cl_2 concentration <0.03 M. In the other experiment, the same amount of chlorine was added in the dark ($[Cl_2]_i \sim 0.1$ M) and then illuminated. The observed selectivities were 18.2 and 19.5, respectively.

In the second set of experiments, the 2,3-dimethylbutane concentration was 0.20 M in 4.0 M benzene (CCl_3F diluent). With initial chlorine concentrations 0.02 M the selectivity is 50.2; with 0.01 M Cl_2 the selectivity is 52.4. In the second, the chlorine was admitted as in the first, but the distance from the light source was 5 times greater. In the third experiment, the chlorine was introduced in the dark ($[Cl_2]_i \sim 0.07$ M) and subsequently illuminated at the same close range as in the first experiment. The selectivities were 96, 88, and 91, respectively; within experimental error, these are the same.

Although earlier studies had demonstrated that interconversions of alkyl radicals (e.g., 1° → 3°) do not occur in chlorinations of alkanes, it was deemed advisable to examine this possibility under our reaction conditions. In no instance was there any indication such rearrangements were occurring. Experiments were run at 0.08 M 2,3-dimethylbutane in CCl_3F, with chlorine concentrations of <0.03 M, and $[Cl_2]_i = 0.07$ and 0.50 M (the excess chlorine was removed with the argon after brief illumination). The observed selectivities were 4.1, 4.2, and 4.8, respectively. Within the time frame permitted by 0.03 M chlorine concentrations, no interconversion of the alkyl radicals is indicated.

A limited examination of the effect of temperature on selectivity was carried out for the 4.0 M CS_2 system (CCl_3F solvent) between 15 and −96 °C. With 5.8 M alkane, temperature has no effect on S. At 0.25 M alkane, the observed selectivity increases sharply with decreasing temperature.

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[1] (a) Russell, G. A.; Brown, H. C. *J. Am. Chem. Soc.* **1955**, *77*, 4034. (b) Russell, G. A. *Ibid.* **1958**, *80*, 4987. (c) Russell, G. A. *Ibid.* **1958**, *80*, 4997.

[2] Walling, C.; Mayahi, M. F. *J. Am. Chem. Soc.* **1959**, *81*, 1485.

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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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(3) Fatool, E., unpublished work, The Pennsylvania State University.

(4) Goldfinger, P.; Huybrechts, G.; Martens, P. *Trans. Faraday Soc.* **1961**, *57*, 2210.

(5) Baxter, H. N., III, unpublished work, The Pennsylvania State University.

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]

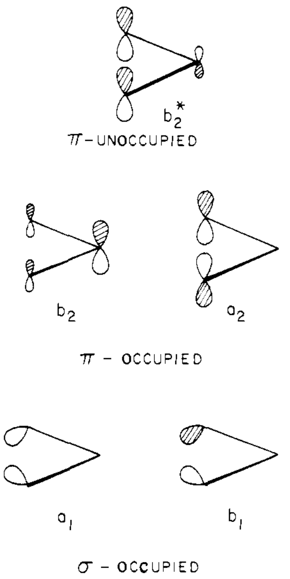

Figure 1. Frontier orbitals of $[C_3H_3]^{3-}$. The hydrogen atoms are not pictured.

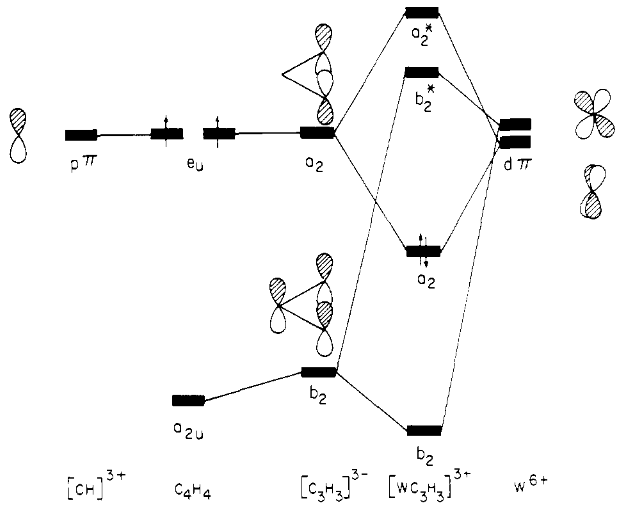

Figure 2. Qualitative MO diagram showing the differences between the interaction of the b_2 and a_2 orbitals of $[C_3H_3]^{3-}$ with the pπ orbital of $[CH]^{3+}$, to form C_4H_4, and the dπ orbitals of W^{6+}, to form $[WC_3H_3]^{3+}$.

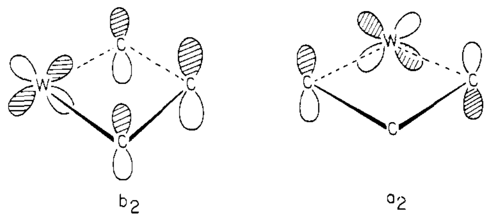

Figure 3. Orbital interactions in the b_2 and a_2 bonding orbitals of $[WC_3H_3]^{3+}$.

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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