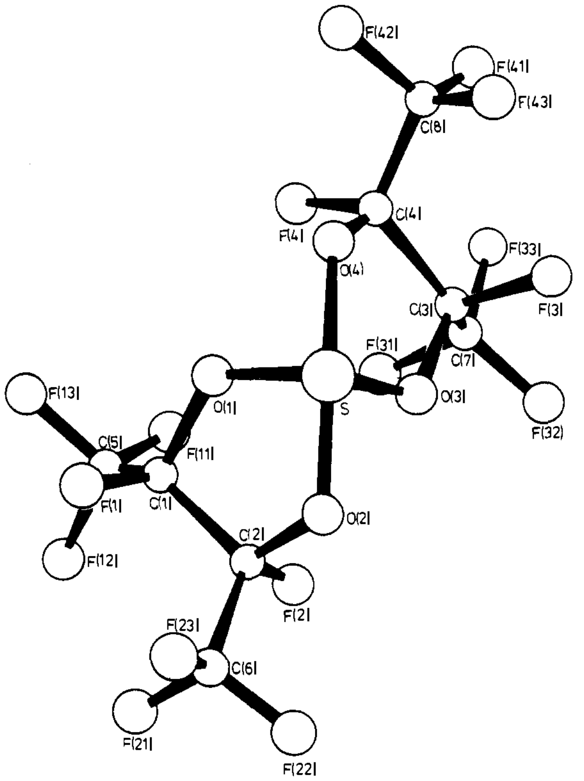

**Figure 1.** Stereoscopic view of a single molecule of **3**; the lone pair of electrons is directed toward the viewer out of the plane of the paper.

of substituents in **3**, rather than cis; for the latter, pseudorotation should lead to positional averaging. These conclusions are supported by the x-ray crystal structure determination (vide infra).

The $^{13}C$ NMR spectra[8] supplement and confirm the findings from the $^{19}F$ spectra. At room temperature two quartets with a shift difference of 0.51 ppm were observed for the carbon atoms of the two $CF_3$ groups. Each line of these quartets, as a result of coupling to the two nonequivalent fluorine substituents, F′, appears as a doublet of doublets.[9] A complicated multiplet is observed for the carbon atoms of the dioxasulfolane rings whose signals partially overlap with those of the $CF_3$ groups. In the $^{13}C$ ($^{19}F_3C$) NMR spectrum, a doublet at 79.2 ppm with still relatively broad lines is observed, $^1J_{CF} = 184.8$ Hz.

The x-ray crystal structure determination of **3** was conducted at −110 °C because of excessive motion of $CF_3$ groups at higher temperatures. **3** forms triclinic crystals, $P1$ or $P\bar{1}$; subsequent refinement has confirmed the latter space group. The cell constants derived from the $2\theta$ settings of 15 strong reflections ($\pm(hkl)$) were as follows: $a = 9.425$ (6), $b = 10.691$ (3), $c = 7.219$ (3) Å; $\alpha = 90.72$ (5), $\beta = 92.65$ (5), $\gamma = 78.57$ (5)°; $z = 2$; calculated density 2.31 g cm$^{-3}$.[10]

The main structural features of **3**, the first tetraoxysulfurane to be studied by x-ray diffraction, may be explained in terms of approximately trigonal-bipyramidal geometry with a stereochemically active lone pair of electrons at sulfur (Figure 1). All the bonds are bent away from the lone pair: $O_{ax}$-S-$O_{ax}$, 171.5 (2)°; $O_{eq}$-S-$O_{eq}$, 104.6 (2)°. The axial S-O bond lengths (1.754 (3) and 1.756 (3) Å, respectively) are significantly shorter than those in some dioxy-diaryl sulfuranes previously studied[11-13] where values ranging between 1.82 and 1.92 Å were observed. Equatorial bond lengths were found as 1.630 (4) and 1.633 (3) Å; no such values for related compounds for comparison are available from the literature. The sulfolane rings are puckered with one carbon atom ~0.35 Å displaced from the plane of the four other ring atoms. The $CF_3$ groups are situated trans to one another in each ring, thus minimizing nonbonded interactions.

Our findings in the $SF_4$/PFBA system suggest that sulfurane formation may be of importance in reactions of $SF_4$ with carbonyl compounds. It has already been established that the reaction of PFBA with sulfur(IV) fluorides may be extended to, for example, $R_2NSF_3$, with similar results. The investigation of the chemistry of **3** and related sulfuranes is in progress.[14]

**Acknowledgments.** We are indebted to NATO Scientific Affairs Division for a grant in support of the study of hypervalent molecules, in collaboration with the late Professor J. I. Musher of Yeshiva University, New York. Support by Deutsche Forschungsgemeinschaft (K.C.H. and J.V.W.) and by Fonds der Chemischen Industrie, Frankfurt am Main, is gratefully acknowledged. Perfluorobiacetyl was generously supplied by Dr. F. Kluge, Höchst A.G., Frankfurt am Main-Höchst, Germany. D.S. thanks Gesellschaft für Biotechnologische Forschung mbH., Stöckheim-Braunschweig, for providing x-ray facilities. Drs. V. Wray and W. S. Sheldrick of the same institution are thanked for $^{13}C$ NMR spectra and assistance with the x-ray structure determination, respectively.

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(3) A number of sulfuranes, including spiro derivatives of a type similar to **3** have been described in the literature; for a recent review see J. C. Martin and E. F. Perozzi, *Science*, **191**, 154 (1976).

(4) Calcd for $C_8F_{16}O_4S$: C, 19.37; F, 61.27. Found: C, 19.50; F, 60.80.

(5) The ion of highest mass number corresponded to *m/e* 477, originating from loss of fluorine from the parent molecule. Besides, numerous other characteristic fragments were observed.

(6) For $^{19}F$ nmr spectra internal $CCl_3F$ was used as a standard. Acetone was used as a solvent for the $^{19}F$ NMR measurements. Very slow decomposition of **3** was noted in this solvent.

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(8) Acetone-$d_6$ served both as a solvent and standard.

(9) The following parameters were observed: $\delta_{C^1}$ 89.82 ppm ($^1J_{CF} = 285.9$ Hz, $^2J_{CF} = 36.9$ Hz, $^3J_{CF} = 1.4$ Hz), $\delta_{C^2}$ 89.31 ppm ($^1J_{CF} = 286.3$ Hz, $^2J_{CF} = 35.1$ Hz, $^3J_{CF} = 2.7$ Hz).

(10) Intensity data were collected using Mo K$\alpha$ radiation by the $\theta$–$2\theta$ scan technique at a variable scan rate of 4–30°/min, depending on the intensity of the reflection; 2436 unique reflections were measured in the range of $3° \leqslant 2\theta \leqslant 50°$. The positions of all atoms were located by automatic centrosymmetric direct methods (SHELX-76, G.M. Sheldrick). Least-square refinement using 1845 reflections with $F_o > 2.5\sigma(F_o)$ led to reliability factors of $R = 0.067$. $R_w = \sum w^{0.5}|F_o - F_c| / \sum w^{0.5}|F_o| = 0.067$; $R_G = [\sum w|F_o - F_c|^2/\sum wF_o^2]^{0.5} = 0.078$.

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(13) A. Kalman, K. Sasvari, and I. Kapovits, *Acta Crystallogr.*, **B29**, 355 (1973).

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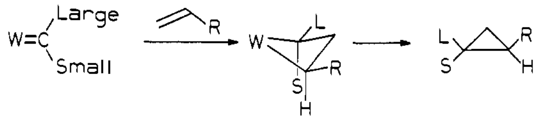
## In Situ Generation and Reactions of $(CO)_5WC(C_6H_5)H$ with Alkenes—Role of Puckered Metallocyclobutanes in Determining the Stereochemistry of Cyclopropane Formation

*Sir:*

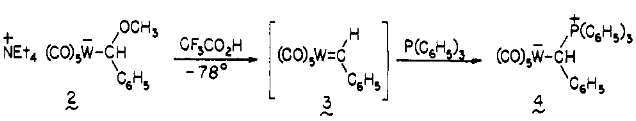
$(CO)_5WC(C_6H_5)_2$ (**1**) reacts with alkenes to give cyclopropanes, olefin scission products, and new carbene complexes.[1] A mechanistic scheme involving the equilibrium between a metallocyclobutane and a metal complex bearing both an alkene and a carbene ligand was proposed to explain these results. Earlier, a similar equilibration had been suggested by Herrisson and Chauvin[2] as a sufficient mechanism for the olefin metathesis reaction.[3] The recent demonstrations that the olefin metathesis reaction proceeds via a nonpairwise exchange of alkylidene groups is consistent with the equilibration between a metallocyclobutane and a metal complex bearing both carbene and alkene ligands and excludes mechanisms requiring the pairwise exchange of alkylidene groups of a pair of alkenes complexed to a metal.[4]

Earlier we pointed out that the moderate stereospecificity observed in the metathesis of 2-pentenes[5] can be explained in terms of the formation of the more stable puckered metallocyclobutane in which repulsive, 1,3-diaxial interactions are minimized.[6,7] In addition, the puckered metallocyclobutane hypothesis predicts the preferential formation of cis cyclopropanes from the reaction of a "large-small" carbene complex with a 1-alkene.[6] Our initial attempts to test the puckered metallocyclobutane hypothesis were frustrated by the rapid decomposition of $(CO)_5WC(C_6H_5)CH_3$ via facile $\beta$-hydride elimination from the methyl group.[6] Here we report the generation of $(CO)_5WC(C_6H_5)H$ (which is not subject to decomposition by a similar pathway) and its reactions with alkenes to give cyclopropanes.



Reaction of $(CO)_5WC(OCH_3)C_6H_5$[8] with $K^+HB[OCH(CH_3)_2]^-$[9] in THF at 0 °C followed by addition of $NEt_4^+Br^-$ gave an 86% yield of $NEt_4^+(CO)_5WCH(OCH_3)C_6H_5^-$ (**2**) as moderately air-sensitive yellow crystals.[10] In an attempt to prepare (phenylcarbene)pentacarbonyltungsten(0) (**3**), 3 equiv of $CF_3CO_2H$ was injected into a 0.01 M solution of **2** in $CH_2Cl_2$ at −78 °C. The solution immediately became dark red[11] and then faded to light orange upon warming to 0 °C. *trans*-Stilbene was the major (43% yield) organic product observed by gas chromatography. Although we have thus far been unable either to isolate or to spectrally observe **3**, evidence consistent with the formation of **3** at −78 °C has been obtained from phosphine trapping experiments and from in situ reactions with alkenes.

The reaction of **2** with $CF_3CO_2H$ in $CH_2Cl_2$ in the presence of $P(C_6H_5)_3$ gave zwitterion **4** in 90% yield.[12] Transition metal-carbene complexes characteristically react with phosphines to give adducts analogous to **4**.[13]

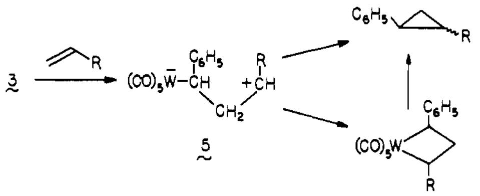


When 3 equiv of $CF_3CO_2H$ were added to a 0.01 M solution of **2** containing 15% by volume alkene at −78 °C, the only organic products obtained were cyclopropanes[14] and *trans*-stilbene (Table I). In the reaction with isobutylene, the red color attributed to **3** faded within 5 min at −78 °C, whereas in the absence of isobutylene the red color persisted for more than an hour at −78 °C. When a mixture of propene (47.3 mmol) and isobutylene (1.72 mmol) were allowed to compete for **3** (0.09 mmol), the ratio of 1-methyl-2-phenylcyclopropanes to 1,1-dimethyl-2-phenylcyclopropane formed was found to be 13.0. The 350-fold greater reactivity of **3** toward isobutylene than toward propene is characteristic of an electrophilic attack[15] of the carbene complex upon the alkene and suggested that a zwitterionic intermediate **5** might be initially formed and then react further to give a metallocyclobutane or a cyclopropane.

**Table I.** Products From the Reaction of $^+NEt_4(CO_5)W^-CH(OCH_3)C_6H_5$ (**2**) with $CF_3CO_2H$ in the Presence of Alkenes[a]

| Alkene | Phenylcyclopropanes, %[b] | syn/anti isomer ratio | *trans*-Stilbene |
|---|---|---|---|
| $(CH_3)_2C{=}CH_2$ | 98 | | <1 |
| $CH_3CH{=}CH_2$ | 80 | 2 | 17 |
| $C_6H_5CH{=}CH_2$ | 39 | 9 | 17 |
| $(CH_3)_3CCH{=}CH_2$ | 69 | <0.01 | 2 |
| *cis*-$CH_3CH{=}CHCH_3$ | 60 | 40[c] | 24 |
| *trans*-$CH_3CH{=}CHCH_3$ | 82 | *d* | 7 |

[a] $CF_3CO_2H$ (3 equiv) was added to a 0.01 M solution of **2** and alkene (~15% vol) in $CH_2Cl_2$ at −78 °C. The reactions were stirred for 1-3 h and then allowed to warm to room temperature. [b] Yields were determined by GC. Products were identified by comparison of GC retention times and NMR spectra with those of authentic samples. [c] A 40:1 ratio of *syn*-1-phenyl-*cis*-2,3-dimethylcyclopropane and *anti*-1-phenyl-*cis*-2,3-dimethylcyclopropane was observed. [d] The only cyclopropane observed was 1-phenyl-*trans*-2,3-dimethylcyclopropane.



To test for such a zwitterionic intermediate, the reaction of **3** with 3,3-dimethyl-1-butene was investigated. The intervention of **5** would be expected to lead to products derived from methyl migration to the carbonium ion center of **5**. However, the reaction of **2** with $CF_3CO_2H$ in the presence of 3,3-dimethyl-1-butene gave 69% *trans*-1-*tert*-butyl-2-phenylcyclopropane, 2% *trans*-stilbene, and no rearrangement products. This result implies that the reaction of **3** with alkenes leads in a concerted manner to either an intermediate metallocyclobutane or directly to a cyclopropane. The finding that both *cis*- and *trans*-2-butene react to give cyclopropanes with retention of the alkene geometry also supports this conclusion.

The exclusive formation of cyclopropanes in the reactions of **3** with alkenes precluded the direct determination of the stereoselectivity of the alkylidene exchange process related to the olefin metathesis reaction. However, the stereochemistry of the cyclopropanes formed gives information about the stereochemical preference of metallocyclobutanes which are considered to be intermediates in both cyclopropanation and olefin metathesis. The reaction of **3** with propene, styrene, and *cis*-2-butene led to the predominant formation of the thermodynamically less stable syn cyclopropanes. This result can be readily interpreted in terms of formation of the more stable puckered metallocyclobutene intermediate.

There are a number of striking differences between the chemistry of the diphenylcarbene complex **1** and of the phenylcarbene complex **3**: (1) **3** reacts with alkenes at −78 °C, while **1** must be heated to 40 °C where CO exchange of **1** is occurring; (2) **3** reacts with alkenes to give cyclopropanes, while **1** gives both cyclopropanes and metathesis products; (3) **3** is more reactive toward isobutylene than toward terminal alkenes, while **1** shows the opposite reactivity pattern. These differences are interpreted in terms of a direct reaction of **3** with an alkene to give a seven coordinate metallocyclobutane which can readily lose $W(CO)_5$ to form cyclopropanes. In contrast, the reaction of **1** with alkenes requires prior dissociation of CO and coordination of an alkene to give a six-coordinate carbene-alkene-metal complex which can reversibly form a six-coordinate metallocyclobutane and give metathesis products. Formation of cyclopropanes from **1** may well require association of an additional ligand to form a seven-coordinate metallocycle so that $W(CO)_5$ may be eliminated rather than the much less stable $W(CO)_4$ fragment. The direct reaction of alkenes with **3** is much faster than the direct reaction with **1** owing to the greater electrophilicity of the phenylcarbene complex and to its lesser steric hindrance.[18]

**Acknowledgment.** This research was supported by the National Science Foundation and by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

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(12) Spectral data: IR (THF) $\nu_{CO}$ 2052 (w), 1962 (w), 1911 (s), 1881 (m); NMR ($CDCl_3$) $\delta$ 7.57 (m, 15 H, $Ph_3P^+-$), 6.97 (m, 5 H, $C_6H_5$), 3.82 (d of t, 1 H, $J_{^{31}P-H}$ = 15.6 Hz, $J_{^{183}W-H}$ = 6.4 Hz). Anal. Calcd for $C_{30}H_{21}O_5PW$: C, 53.28; H, 3.13; W, 27.18. Found: C, 53.28; H, 3.20; W, 26.55.

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(15) In contrast, nucleophilic tantalum–carbene complexes react with alkenes to give products derived from initial bonding of the carbene to the least substituted carbon of the alkene.[16] Gassman has explained the reactions of ethylcyclopropane with terminal alkenes in the presence of a metathesis catalyst in terms of a nucleophilic carbene complex.[17]

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(18) **Note Added in Proof.** The 270-MHz NMR spectrum of a 0.009 M solution of **3** at −68 °C shows a singlet at $\delta$ 17.21 for the hydrogen attached to the carbene carbon atom. The NMR spectra of similar isolated phenylcarbene–iron complexes has been observed.[19]

(19) M. Brookhart and G. O. Nelson, *J. Am. Chem. Soc.*, following paper in this issue.

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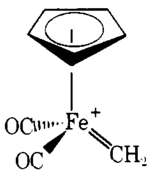
## Isolation of Stable Secondary Cationic Iron Carbene Complexes $\eta^5$-$C_5H_5(CO)_2FeCHC_6H_5PF_6$ and $\eta^5$-$C_5H_5(CO)[P(C_6H_5)_3]FeCHC_6H_5PF_6$

*Sir:*

The majority of transition metal-carbene complexes prepared to date have contained at least one heteroatom directly bound to the carbene carbon atom.[1] Such groups serve as electron-donating substituents to the electrophilic carbene carbon atom and provide substantial stabilization to these types of complexes. Recently several carbene complexes have been described which lack heteroatom stabilization.[2-6] Such complexes have generated considerable interest due to their potentially higher chemical reactivity and specifically due to their probable intermediacy in the olefin metathesis reaction.[7] Examples of such species include the Cp(benzocyclobutenylidene) iron dicarbonyl cation,[2] $(CO)_5W{=}C(C_6H_5)_2$,[3] $Cp(CO)_2Mn{=}CR_1R_2$ ($R_1,R_2$ = phenyl or methyl),[4,5a,6] $Cp(CO)_2Mn{=}C(C_6H_5)(COC_6H_5)$,[6] and several complexes of the type $(CO)_5M{=}CR_1R_2$ (M = W or Cr; $R_1$, $R_2$ = aryl, thienyl, or furyl) reported by Fischer.[5c]

In a series of recent papers, Schrock has reported a number of remarkably stable neutral alkylidene–tantalum complexes in which the carbene carbon atom appears nucleophilic in nature.[8] These complexes include the first isolated unsubstituted methylene complex $Cp_2(CH_3)Ta{=}CH_2$[8b] and the first reported secondary alkylidene complexes $(Cp)_2(C_6H_5CH_2)Ta{=}CHC_6H_5$ and $[(CH_3)_3CCH_2]_3Ta{=}CH[C(CH_3)_3]$.[8a,d]

We wish to report here some recent observations regarding nonheteroatom-stabilized cationic iron–carbene complexes. Our work in this area was prompted by earlier observations of Pettit and Jolly[9] and Green.[10] Pettit reported that treatment of $Cp(CO)_2FeCH_2OCH_3(FpCH_2OCH_3)$, **1**, with $HBF_4$ in the presence of cyclohexene led to norcarane.[9,11] The intermediacy of the cationic methylene complex, **2**, was suggested. Both Pettit[9] and Green[10] have reported that treatment of ether complex, **1**, with strong acids at 25 °C in the absence of olefins led to mixtures of iron complexes which were not readily separated and which always included the cationic ethylene complex, $Fp(CH_2CH_2)^+$. Again the cationic methylene complex **2** was judged a reasonable intermediate to account for the observed chemistry and for the formation of the ethylene complex.



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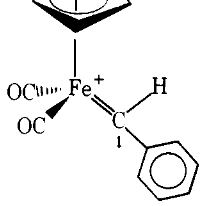
In an effort to observe **2** we have carried out a low temperature protonation of **1**. Treatment of a solution of $HSO_3F$-$SO_2ClF$ at −100 °C with a cooled (−100 °C) solution of **1** in $CD_2Cl_2$ resulted in formation of a deep red solution. Immediate examination of the $^1H$ NMR spectrum of this solution at −80 °C revealed that a clean disproportionation had occurred with formation of equimolar amounts of $FpC_2H_4^+$[12] and $CpFe(CO)_2^+$.[13] If the methylene complex **2** is formed in this reaction, then disproportionation occurs quit rapidly even at −80 °C.

Success in preparing secondary derivatives of this class of nonheteroatom-stabilized carbene complexes was achieved through phenyl substitution at the carbene carbon atom. Treatment of $FpCH(C_6H_5)OCH_3$, **3**, at low temperatures (<−10 °C) with trifluoroacetic, fluorosulfonic, or triflic acid resulted in deep orange solutions of the benzylidene complex **4**. The $^1H$ NMR of **4** at −25 °C in triflic acid shows resonances at $\delta$ 16.86 (1 H, s, $C_1$ H), 7.70–8.13 (5 H, br m, $C_6H_5$), and



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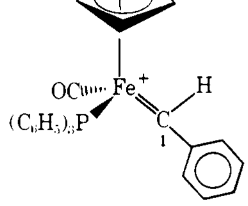

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