In summary, this simple analysis allows one to expand beyond the one-dimensional limitation of the earlier model. The conclusions are consistent with the current knowledge of the binding site. Furthermore, the model successfully explains new, unusual analogue results. Continued effort will be directed toward a better understanding of restrictions in the third dimension of the binding site.

Note Added in Proof. The pivotal motion of the α,β-bond about the C_α atom probably should be more restricted than what is permitted by the current model, correctly suggested to us by Prof. R. Birge. However, models show that such a refinement has no effect on the conclusions reached in the current study.

Supplementary Material Available: Photographs of molecular models of all remaining 15 isomers of the confined butyl retinylidene chromophore and ^{1}H NMR data (δ, J, and NOE) of isomers of 12-methyl- and 12-chlororetinal (3 pages). Ordering information is given on any current masthead page.

Control of Olefination Stereochemistry Using Long-Chain Zirconium Alkylidene Analogues of the "Tebbe" Reagent

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The Tebbe compound,[1] $Cp_2Ti(CH_2)ClAlMe_2$, has been shown to be a reagent of general synthetic utility for methylene group transfer to a range of organic carbonyls.[2] In these reactions, since only CH_2 is transferred, the problem of controlling stereochemistry of olefination does not exist. Using long-chain alkylidene analogues[3,4] of the Tebbe reagent, however, raises this as an important issue. Observations concerning "Wittig-type" reactivity of the Tebbe reagent or its analogues suggested a stepwise olefination process involving an intermediary metallooxetane which then fragments to give the metal oxo complex and the olefinic product.[5] It could be that stereochemical factors leading to the preferential formation of either possible metallooxetane from an *unsymmetrically*-substituted metal carbene complex control the product distribution of olefins thus formed. The oxygen atom in the metallooxetane may not provide much differentiating stereochemical information and, therefore, may not be of much use in controlling formation of either metallooxetane or ultimate product distribution. Replacing (=O) with a (=NR) group, however, might provide one method to control stereochemistry in an olefination sequence: the imine, which contains a sterically significant group on nitrogen, would give rise to an N-substituted metallazetidine structure, and the ring that is preferentially formed may be the one that minimizes steric interactions among all *four groups* of the four-membered ring. With this concept in mind, we have studied reactions between substituted zirconium carbene complexes and imines and find that not only does olefination occur but also that a correlation exists between the E/Z selectivity of olefins formed and the size of the substituent group on imine nitrogen.

(1) Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978,** *100,* 3611.
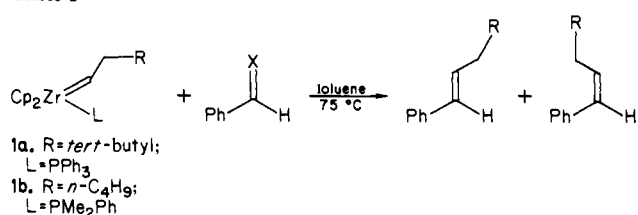
(2) Pine, S. H.; Zahler, R.; Evans, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1980,** *102,* 3270.

(3) Hartner, F. W., Jr.; Schwartz, J. *J. Am. Chem. Soc.* **1981,** *103,* 4979.

(4) Hartner, F. W., Jr.; Schwartz, J.; Clift, S. M. *J. Am. Chem. Soc.* **1983,** *105,* 640.

(5) Kauffmann, T.; Ennen, B.; Sander, J.; Wieschollek, R. *Angew. Chem., Int. Ed. Engl.* **1983,** *22,* 244.

Table I

1a. R = *tert*-butyl;
L = PPh$_3$
1b. R = *n*-C$_4$H$_9$;
L = PMe$_2$Ph

carbene	X	"A"^{c}	E/Z	h at 75 °C	olefin yield, %^{a,b}
1a	=O		0.50	3	76
	=NCH$_3$	1.8	2.06	3	88
	=NCH(CH$_3$)$_2$	2.1	2.30	4	47
	=NPh	3.1	2.76	3	56
	=NC(CH$_3$)$_3$	>4.5	4.32	2	16
1b	=O		1.11	5	72
	=NCH$_3$	1.8	1.13	5	85
	=NCH(CH$_3$)$_2$	2.1	1.67	5	39

^{a} Based on carbene; product ratios were determined by VPC analysis; products were isolated by preparative VPC and structures were confirmed by comparison with authentic materials. ^{b} **1** slowly dimerizes under these conditions;[4] no carbene complex remained; the unreacted imine can be recovered unchanged. ^{c} For substituents on N.[12]

Table II
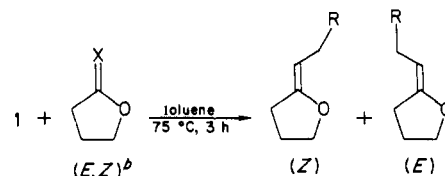
carbene	X	E/Z	enol ether yield, %^{a}
1a	=O	1.00	71
	=NPh	0.53	72
1b	=O	1.04	80
	=NPh	0.35	91

^{a} Based on carbene complex, determined by VPC. ^{b} 1:2.3 ratio.

In a typical olefination procedure benzaldehyde (1 equiv) was added to a toluene solution of **1a**[4] (0.062 M) at 25 °C; the reaction mixture was then heated to 75 °C for 3 h. A preference for formation of the Z isomer of the olefin was noted as it is in "salt-free" Wittig reactions[6] using triphenylphosphoranes.[6b] In contrast, using the imines shown in Table I this E/Z selectivity can be reversed.[7] In each case, procedures were identical with the one noted for benzaldehyde. For example, N-methyl-benzylideneimine (1 equiv) was added to a toluene solution of **1a**[4] (0.062 M) at 25 °C, followed by heating to 75 °C for 3 h. A preference for the E isomer of the olefin was noted.

The Tebbe reagent is especially useful in that it can methylenate esters to give enol ethers.[2] We had noted that zirconium carbene complexes likewise react readily with esters.[4] Consistent with the observations described for imines, we observe that imidates[8] also react with zirconium carbene complexes to yield enol ethers. Here, as in the case of the imines described above, by use of an N-substituted imidate, E/Z selectivity of the olefin formed can be controlled (see Table II).

Reactions discovered between zirconium carbene complexes and imines or imidates (and thioketones) expand in scope the nature of substrates that can react with group 4 carbene complexes to give olefins. The fact that a sterically significant group can be utilized in conjunction with a "throwaway" part of the substrate

(6) (a) Vedejs, E.; Meier, G. P.; Snoble, K. A. J. *J. Am. Chem. Soc.* **1981,** *103,* 2823. (b) Schlosser, M.; Schaub, B. *J. Am. Chem. Soc.* **1982,** *104,* 5821.

(7) Thioketones also react with zirconium carbene complexes to yield olefins. However, the E/Z selectivity for olefin formation is essentially identical with that noted for the carbonyl compound itself.

(8) Mukaiyama, T.; Sato, K. *Bull. Chem. Soc. Jpn.* **1963,** *36,* 99.

to control the stereochemistry of product formation enhances the synthetic utility of these procedures. Further stereochemical studies in this area could shed light on geometrical considerations for likely metallazetidine intermediates.[9]

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(9) For aldehydes, only one isomer of the imine is noted; for the imidate, both *E* and *Z* isomers exist in comparable amounts,[10,11] and four metal-azetidines are therefore possible.

(10) Deyrup, J. A.; Gingrid, H. L. *J. Org. Chem.* **1977**, *42*, 1015.

(11) Saito, H.; Nukuda, K. *Tetrahedron* **1966**, *22*, 3313.

(12) Carey, F. A.; Sundberg, R. J. "Advanced Organic Chemistry"; Plenum Press: New York, 1977; Chapter 3.


Perfluorobicyclo[4.2.0]octa-2,4,7-triene: A Labile (CF)₈ Valence Isomer

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We wish to report the synthesis, characterization, and some of the chemistry of the title compound (**2**), the elusive bicyclic valence isomer of perfluorocyclooctatetraene (**1**). As is the case with cyclooctatetraene itself,[2] the bicyclic isomer is present in such small amount at equilibrium that it has never been detected directly in samples of the tetraene (eq 1). Its existence has been
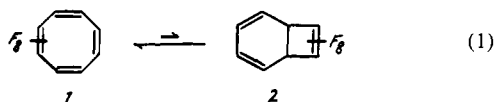
implied, however, by the reaction of **1** with dienophiles to give adducts such as **3**,[3] which are (formally, at least) Diels–Alder adducts of **2**. In addition, ultraviolet irradiation of the tetraene yields a 20:1 mixture of tricyclo[4.2.0.0²,⁵]octa-3,7-dienes **4** and **5**, a result most easily understood in terms of **2** as an intermediate (formed either thermally or photochemically).[4]
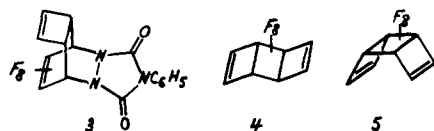
Starting with perfluorobenzene (**6**), we have now synthesized bicyclic triene **2** in five steps (Scheme I). Photocycloaddition of **6** to dichlorodifluoroethylene proceeded in [2 + 2] fashion to yield **7**, which photocyclized under the reaction conditions to give a stereoisomeric mixture of anti tricyclic adducts **8**.[5] Dechlorination of **8** was accomplished with activated zinc dust in dimethyl sulfoxide under the influence of ultrasound at room temperature and reduced pressure (58% yield after recrystallization from isopentane).[6] *We have found this combination to be remarkably*

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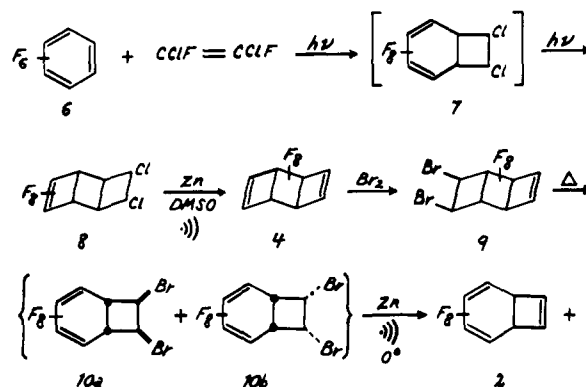
(2) Huisgen, R.; Mietzsch, F. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 83–85. Huisgen, R.; Mietzsch, F.; Boche, G.; Seidl, H. *Spec. Publ.—Chem. Soc.* **1964**, *19*, 3–20.

(3) Seiders, B. B., unpublished work from this laboratory.

(4) Barefoot, A. C., III; Saunders, W. D.; Buzby, J. M.; Grayston, M. W.; Lemal, D. M. *J. Org. Chem.* **1980**, *45*, 4292–4295.

(5) Lemal, D. M.; Buzby, J. M.; Barefoot, A. C., III; Grayston, M. W.; Laganis, E. D. *J. Org. Chem.* **1980**, *45*, 3118–3120.

Scheme I

effective for vicinal dechlorination of chlorofluorocarbons.[9] The resulting *unti*-tricyclooctadiene **4** reacted stereospecifically with bromine to give the known cis,exo dibromide **9** together with the doubly cis,exo tetrabromide, from which it is easily separated.[4] Replacement of chlorines by bromines was essential in order that the final step in the sequence be performable under the mildest possible conditions. Thermolysis of **9** at 160 °C yielded an 87:13 mixture of stereoisomeric dienes **10a** and **10b** (95% after distillation). The presence of endo isomer **10b** reveals that the initially formed exo diene **10a** ring opened to monocyclic triene **11**, which recyclized to produce both dienes (eq 2). None of the monocyclic isomer could be detected in the product mixture.[10]
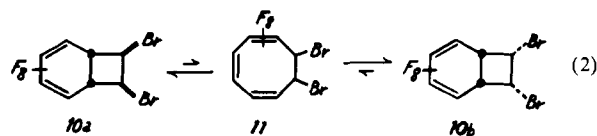
At temperatures near 0 °C the major isomer **10a** crystallized, allowing separation from **10b**. Spectroscopic data for **10a**:[11] IR (neat) 1750, 1705, 1405, 1350, 1325, 1190, 1030, 850 cm⁻¹; UV (cyclohexane) λ_{max} 281 nm (log ϵ = 3.43); ¹⁹F NMR (CDCl₃)[12] 123.5, 148.4, 154.6, 157.7 ppm, for **10b**, 126.6, 148.4, 154.6, 181.3 ppm.[13]

In the culminating step, **10** was debrominated with activated zinc dust in 1:1 dimethyl sulfoxide/*N*-methylpyrrolidinone in an ultrasonic bath at 0 °C and 0.05 torr. Under these conditions bicyclic triene **2** distilled as it was formed into a U-trap at −196 °C, together with a minor amount of tetraene **1**. With care an 82:18 mixture of triene/tetraene could be obtained in 74% yield. The identity of the bicyclic triene was revealed by the spectroscopic data described below and by its quantitative isomerization to perfluorocyclotetraene at subambient temperatures. Measured at −60 °C in methylene chloride, the ¹⁹F NMR spectrum comprised four multiplets of equal area at 118.3 (F₇,F₈), 150.4 (F₃,F₄), 154.5 (F₂,F₅), and 159.1 ppm (F₁,F₆). The infrared spectrum, determined in an argon matrix at 20 K, revealed bands at 1773

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(6) This appears to be the first report of an ultrasound-assisted vicinal dehalogenation by zinc. The zinc/ultrasound combination has been used by others, however, to generate *o*-xylylene from α,α′-dibromo-*o*-xylene[7] and to prepare organozinc reagents.[8]

(7) Han, B.-H.; Boudjouk, P. *J. Org. Chem.* **1982**, *47*, 751–752.

(8) Kitazume, T.; Ishikawa, N. *Chem. Lett.* **1982**, 137, 139; **1981**, 1679. Han, B.-H.; Boudjouk, P. *J. Org. Chem.* **1982**, *47*, 5030–5032.

(9) Steffen, M. A.; Ralli, P.; Sharos, C. J.; Secor, E. A., unpublished work from this laboratory.

(10) For analogous valence isomerizations in the hydrocarbon series, see: Huisgen, R.; Boche, G.; Dahmen, A.; Hechtl, W. *Tetrahedron Lett.* **1968**, 5215–5219. Huisgen, R.; Boche, G. *Ibid.* **1965**, 1769–1774.

(11) A satisfactory elemental analysis was obtained (Galbraith Laboratories, Inc., Knoxville, TN).

(12) Chemical shifts are reported in parts per million upfield from internal trichlorofluoromethane.

(13) The contrast in chemical shift of the bridgehead fluorines in the two isomers (157.7 vs. 181.3 ppm) forms the basis for the configurational assignment, as the lower field position is characteristic of bridgehead fluorines vicinal to exo bromines in perfluorotricyclo[4.2.0.0²,⁵]octane derivatives.[4]