known[2] tetracyclic ketone **2**. Chromatography[12a] afforded 133 mg (78% yield) which, as shown by GC coinjection experiments, consisted of a 58:42 mixture of **2** and its 17α epimer. The GC response for these epimers (with "natural" configuration) represented 95% of the total peak area while that for the 13α,17β isomer was only 2% and for the 13α,17α, 1.5%; moreover, there was no response for the *D*-homo isomer.

Thus a dramatic improvement in regio- as well as stereoselectivity, with commensurate increase in yield, was realized when the vinyl fluoride was used in place of the methylacetylenic function for terminating a biomimetic polyene cyclization.

Acknowledgments. We are indebted to the National Institutes of Health and the National Science Foundation for support of this research. T.A.L. was the recipient of an NIH postdoctoral fellowship and M.N. was supported by Fijisawa Pharmaceutical Co., Ltd. We also wish to express appreciation to Dr. G. A. Boswell, Jr., of Du Pont for helpful discussions and for a generous gift of (diethylamino)sulfur trifluoride.

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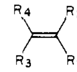
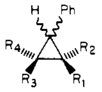
Reactions of η^5-$C_5H_5(CO)_2FeCHC_6H_5^+$ with Alkenes and Alkynes. Observation of Efficient Benzylidene-Transfer Reactions

Sir:

The transfer of carbene ligands from transition-metal–carbene complexes to alkenes with formation of cyclopropanes represents a general class of reactions with considerable potential synthetic utility. Unfortunately, however, few of the stable, isolable carbene complexes prepared to date exhibit this mode of reactivity.[1] The most notable exception is the report by Casey that $(CO)_5WCHC_6H_5$ generated in situ (trifluoroacetic acid–methylene chloride solutions) reacts with numerous substituted alkenes to form phenylcyclopropanes.[2,3] Several systems of the type $CpLL'FeCH_2X$ have been used as methylene-transfer reagents[4] in which the cationic methylene complex is an unsubstantiated but plausible intermediate and, indeed, $Cp(Ph_2PCH_2CH_2PPh_2)FeCH_2^+$ generated in situ is capable of methylene transfer.[10]

Table I. Products of the Reaction of Alkenes with $Cp(CO)_2Fe{=}CHC_6H_5^+$

alkene	cyclopropane product[a]	cis:trans isomer ratios	% yield[b] GC	iso-lated
				
$R_1 = R_2 = R_3 = R_4 = H$			75	47
$R_1 = CH_3$; $R_2 = R_3 = R_4 = H$		7.8 (0 °C)[c]	90	54
$R_1 = CH_2CH_3$; $R_2 = R_3 = R_4 = H$		6.5 (0 °C)[c]		75
$R_1 = CH(CH_3)_2$; $R_2 = R_3 = R_4 = H$		4.6 (0 °C)[c]		76
$R_1 = C_6H_5$; $R_2 = R_3 = R_4 = H$		≥100[d]		88
$R_1 = R_4 = CH_3$; $R_2 = R_3 = H$		[f]	89	52
$R_1 = R_3 = CH_3$; $R_2 = R_4 = H$		>100[e]	93	57
$\overline{R_1 \quad R_3} = CH_2CH_2CH_2$ (cyclopentene); $R_2 = R_4 = H$		≥200[d] (endo:exo)		78
$R_1 = R_2 = CH_3$; $R_3 = R_4 = H$			82	45
$R_1 = R_2 = C_6H_5$; $R_3 = R_4 = H$				75
$R_1 = R_4 = C_6H_5$; $R_2 = R_3 = H$		[f]		96
$R_1 = R_2 = R_3 = CH_3$; $R_4 = H$		>50		91
$R_1 = R_2 = R_3 = R_4 = CH_3$				59

[a] Reaction conditions are described in the text. [b] Yields are based on carbene salt. Isolated yields are reported after bulb-to-bulb distillation of oils or recrystallization of solids. Isolated yields of volatile products are low relative to GC yields due to loss in distillation of small quantities. [c] Carried out at a constant temperature (0 °C) for accurate comparison of isomer ratios. Selectivity increases at lower temperatures. [d] Minor isomer detected by GC but not otherwise characterized. [e] Refers to the *r*-1-phenyl-*cis*-2,*cis*-3-dimethylcyclopropane:*r*-1-phenyl-*trans*-2,*trans*-3-dimethylcyclopropane ratio. [f] No isomers (<1%) detected corresponding to isomerization about the double bond.

We report here that the highly electrophilic benzylidene iron carbene complex $Cp(CO)_2FeCHC_6H_5^+$, **1**, which can be readily isolated as a stable crystalline PF_6^- salt,[11] reacts rapidly with unactivated alkenes and alkynes to effect efficient transfer of the benzylidene ligand. Table I summarizes the results of the reaction of **1** with alkenes to form phenylcyclopropanes. In a typical procedure, a twofold excess of olefin is added to the carbene salt **1** in methylene chloride at −78 °C. After 1−2 h of stirring at −78 °C the solution is slowly warmed to 25 °C. Pentane is added to precipitate iron-containing salts[12] and after filtration and solvent removal the phenylcyclopropanes can be isolated in good yields.

There are two remarkable features of these reactions. First, carbene complex **1** is sufficiently electrophilic to react with unactivated ethylene,[13] yet steric factors do not prevent transfer to tetrasubstituted olefins. Thus, good yields of phenylcyclopropanes may be obtained for olefins ranging from unsubstituted ethylene to tetrasubstituted systems. Secondly, the reaction is highly stereoselective, giving exceptionally high fractions of the thermodynamically less stable cis or syn isomers. For example, from styrene the cis:trans ratio of 1,2-diphenylcyclopropane formed was ≥100 while for cyclopentene was ≥200. The stereoselectivity of the iron carbene **1** seems for all olefins to be considerably greater than that for the $(CO)_5WCHC_6H_5$ system,[2] but the relative stereoselectivities of the two complexes generally parallel one another.[14]

By what mechanism(s) are the cyclopropanes formed and how can the high stereoselectivities be explained? The addition of **1** to olefins to form carbonium ion intermediates seems unlikely since

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(1) For recent reviews of transition-metal–carbene complexes, see: (a) Casey, C. P. *Transition Met. Organomet. Org. Synth.* **1976**, *1*, 190–233. (b) Cardin, D. J.; Cetinkaya, B.; Doyle, M. J.; Lappert, M. F. *Chem. Soc. Rev.* **1973**, *2*, 99–144. (c) Fischer, E. O. *Adv. Organomet. Chem.* **1976**, *14*, 1–32. (d) Cotton, F. A.; Lukehart, C. M. *Prog. Inorg. Chem.* **1972**, *16*, 487–613.

(2) (a) Casey, C. P.; Polichnowski, S. W. *J. Am. Chem. Soc.* **1977**, *99*, 6097–9. (b) Casey, C. P.; Polichnowski, S. W.; Shusterman, A. J.; Jones, C. R. *J. Am. Chem. Soc.* **1979**, *101*, 7282–92.

(3) (a) The heteroatom carbene complexes $(CO)_5MC(OCH_3)(C_6H_5)$ (M = W, Mo, Cr) react at high temperatures with certain electron-deficient olefins and under mild conditions with electron-rich olefins to yield cyclopropanes.[3b] The reactions likely proceed by different mechanisms[1a] and do not appear to be general for unactivated olefins. (b) Dötz, K. H.; Fischer, E. O. *Chem. Ber.* **1972**, *105*, 1356–67, 3966–73.

(4) The α-ethers $Cp(CO)_2FeCH_2OCH_3$[5] and $Cp(Ph_2PCH_2CH_2PPh_2)FeCH_2OCH_3$[6] and chiral $Cp(CO)(PPh_3)FeCH_2O$-menthyl[7] transfer methylene under acidic conditions while chiral $Cp(CO)(PPh_3)FeCH_2Br$[8] and $Cp(CO)_2FeCH_2S^+(CH_3)_2$[9] transfer methylene thermally. The latter reagent appears particularly useful synthetically due to its ease of preparation, stability, and efficient methylene transfer.

(5) Jolly, P. W.; Pettit, R. *J. Am. Chem. Soc.* **1966**, *88*, 5044–5.

(6) Riley, P. E.; Capshaw, C. E.; Pettit, R.; Davis, R. E. *Inorg. Chem.* **1978**, *17*, 408–14.

(7) Davison, A.; Krusell, W. C.; Michaelson, R. C. *J. Organomet. Chem.* **1974**, *72*, C7–C10.

(8) Flood, T. C.; DiSanti, F. J.; Miles, D. L. *Inorg. Chem.* **1976**, *15*, 1910–8.

(9) Brandt, S.; Helquist, P. *J. Am. Chem. Soc.* **1979**, *101*, 6473–5.

(10) Brookhart, M.; Tucker, J. R.; Flood, T. C.; Jensen, J. *J. Am. Chem. Soc.* 1980, *102*, 1203–5.

(11) Brookhart, M.; Nelson, G. O. *J. Am. Chem. Soc.* **1977**, *99*, 6099–101.

(12) These salts have been fully characterized as Fp(olefin)$^+$ salts for the alkenes ethylene and propene but are not normally characterized.

(13) The $(CO)_5WCHC_6H_5$ system does not react with ethylene.[2b]

(14) The increased selectivity of the reaction of **1** with cyclopentene appears to be an exception. Casey reports an endo:exo ratio of 2.6 for $(CO)_5WCHC_6H_5$.[2b]

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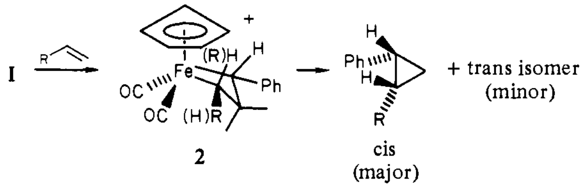
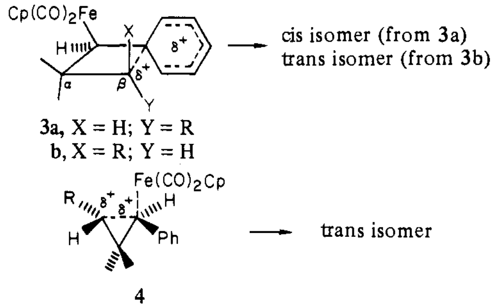
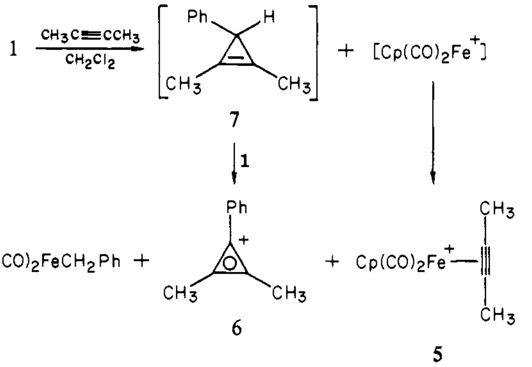
configuration around the double bond is maintained in the product (compare *cis*- and *trans*-2-butenes). Recent evidence has implicated metallacyclobutanes, formed from reactions of metal carbenes and olefins, as intermediates in olefin metathesis.[15] This suggests that a metallacyclobutane intermediate such as **2** (or at least a metallcyclobutane-like transition state) might be involved in the reaction of **1** with alkenes. Models suggest that the Cp ring would direct substituents to lie preferentially cis to one another and anti to the Cp ring in the metallacyclobutane-like transition state, thus ultimately leading selectively to cis products. Two experimental observations speak against this model. First, as the size of the alkyl substituent increases in a series of monosubstituted olefins $CH_2{=}CHR$ (R = CH_3, CH_2CH_3, $CH(CH_3)_2$; see Table I), the selectivity *decreases*. Secondly, we have examined the reaction of the *p*-tolyl complex $Cp(CO)_2FeCH(p\text{-}CH_3C_6H_4)^+$ with propene at 0 °C and have found that the *p*-CH_3 substituent has a significant effect on selectivity, giving a 10:1 cis:trans ratio of (*p*-tolylmethyl)cyclopropane as compared to 7.8:1 for the unsubstituted phenyl case. The effect of the *p*-CH_3 substituent must be electronic and not steric in nature and is inconsistent with the metallacyclic model, where steric interactions control the selectivity.[16]



The most attractive mechanistic model is one proposed by Casey[2] for reactions of $(CO)_5WCHC_6H_5$, in which a special stabilizing role is ascribed to the phenyl ring. Briefly put, the positive charge which develops at the β carbon upon interaction of the alkene with the electrophilic carbene center can be stabilized in the transition state via interaction with the ipso carbon of the phenyl ring, as shown in **3**. In this cyclobutane-like transition state the substituent R prefers to lie predominantly trans to $Cp(CO)_2Fe$, as in **3a**. Upon formation of cyclopropane by electrophilic attack of C_β on the iron–carbon bond, the substituent R ends up cis to the phenyl substituent.[17] To explain the decrease in selectivity with increasing size of alkyl groups in monosubstituted olefins, it is necessary to postulate an "open" transition state, as shown by **4**, which leads to higher fractions of trans product and in which the substituent R is sterically less crowded than in **3**. Thus, in this scheme, as R increases in size, more product is formed via transition state **4**, giving higher fractions of trans cyclopropane. The increased cis:trans selectivity of the *p*-tolyl carbene complex is also consistent with this Casey model since the *p*-CH_3 substituent will clearly stabilize transition state **3** (which leads predominantly to cis product) relative to transition state **4**.



Preliminary experiments indicate that **1** is also highly reactive toward alkynes. Relatively few reactions of metal carbenes with alkynes have been reported[2b,18] and the reactivity patterns observed here appear unprecedented. Treatment of **1** with 3 equiv of 2-butyne in methylene chloride at −78 °C followed by warming to 25 °C results in formation of equimolar ratios of $Cp(CO)_2FeCH_2C_6H_5$, $Cp(CO)_2Fe(CH_3C{\equiv}CCH_3)^+PF_6^-$ (**5**),[19] and 1,2-dimethyl-3-phenylcyclopropenium hexafluorophosphate (**6**) (isolated yields of **5** and **6** were ca. 75%). The reaction likely occurs by initial carbene transfer to form phenyldimethylcyclopropene (**7**) followed by hydride transfer to unreacted **1**.



On the basis of the results presented here, the readily and inexpensively generated carbene complexes of the type $Cp(CO)_2Fe{=}CHR^+$ appear to have substantial synthetic utility for carbene-transfer reactions and we are continuing to examine the chemistry of such species.

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[15] For reviews of olefin metathesis see: Calderon, N.; Lawrence, J. P.; Ofstead, E. A. *Adv. Organomet. Chem.* **1979**, *17*, 449-93. Katz, T. J. *Ibid.* **1977**, *16*, 283-317. Grubbs, R. H. *Prog. Inorg. Chem.* **1976**, *24*, 1-50. Calderon, N.; Ofstead, E. A.; Judy, A. W. *Angew. Chem.* **1976**, *88*, 433-42. Hains, R. J.; Leigh, G. *Chem. Soc. Rev.* **1975**, *4*, 155-88.

[16] (a) Although $(CO)_5WC(C_6H_5)_2$ reacts with alkenes to form metathesis products (presumably via CO dissociation and formation of a metallacyclobutane intermediate),[15b] we see no evidence for metathesis-like products from reaction of **1** with olefins. CO dissociation from **1** under the reaction conditions is quite slow. Generation of a stable metallacycle directly from **1** would require formation of a formally iron(IV) dicarbonyl species which is an electronically unattractive intermediate. (b) Casey, C. P.; Burkhardt, T. J. *J. Am. Chem. Soc.* **1974**, *96*, 7808-9.

[17] As pointed out by Casey,[2b] such a model also explains the high selectivity for 2-methyl-2-butene in that the single methyl group on the α carbon in **3** would prefer to lie trans to Fp.

[18] Dötz, K. H.; Dietz, R. *Chem. Ber.* **1978**, *111*, 2517-26. *Ibid.* **1977**, *110*, 1555-1563. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 644-5.

[19] (a) The properties of this salt were identical with those reported for this complex prepared by a different route.[17b] (b) Reger, D. L.; Coleman, C. J.; McElligott, P. J. *J. Organomet. Chem.* **1979**, *171*, 73-84.

Acepleiadylene Dianion and Tetraanion

Sir:

Cyclohept[*fg*]acenaphthylene (acepleiadylene) (**1**), synthesized in 1956 by Boekelheide,[1] has always attracted special attention since, from thermochemical, spectroscopic, and theoretical arguments, it is strongly believed to exist as a vinyl-bridged [14]-annulene[2] and to thus constitute an example of Platt's perimeter

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[1] V. Boekelheide and G. K. Vick, *J. Am. Chem. Soc.*, **78**, 653 (1956).

[2] (a) R. B. Turner, W. S. Lindsay, and V. Boekelheide, *Tetrahedron*, **27**, 3341 (1971); (b) A. J. Jones, P. D. Gardner, D. M. Grant, W. M. Litchman, and V. Boekelheide, *J. Am. Chem. Soc.*, **92**, 2395 (1970); (c) A. DasGupta and N. K. DasGupta *Theor. Chim. Acta*, **33**, 177 (1974).