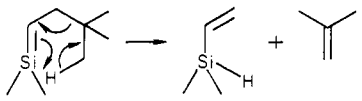
Table I. Results from the Flash Vacuum Pyrolysis of 1 [a] at 550 °C

expt	flow, μL of 1/min	% decompn	% of dimers	2 (cis/trans)	% of isobutene	% of 3	ene/dimer ratio [b]
1	0.7	90	8	1.15	50	40	5.00
2	3.2	76	22	1.15	39	23	1.05
3	30.0	83	48	1.14	19	12	0.25
4 [c]	7.0	36	36	1.15	36	25	0.69

[a] Percent yields determined by VPC using di-*n*-butyl ether as an internal standard. [b] Based on yield of 3/yield of 2. [c] Pyrolysis carried out in the presence of a 6-fold excess of methylene chloride.

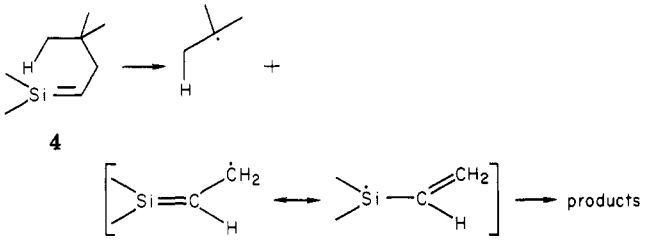
products at 550 °C. Based on the evidence presented below, we propose that these products arise from a unimolecular ene reaction of 4.



4 3

If dimerization is second order in silene while the ene reaction is first order in silene, one would predict the dimerization to be favored over the ene reaction with increasing silene concentration. The results in Table I support this hypothesis. With increasing flow rates and therefore increasing silene concentration, the ratio of disilacyclobutanes to dimethylvinylsilane increases 20-fold. At low flow, 3 is obtained in 5 times greater yield than the dimers 2; at high flow, the situation is reversed, with dimers being produced in yields 4 times greater than the ene product. Thus, dimethylvinylsilane production is clearly of lower kinetic order than the case for silene dimerization and is most probably first order.

In addition to the ene pathway for the formation of 3, a radical mechanism, involving a rate-determining homolysis of the carbon–carbon bond β to silicon in the silane, 4, followed by hydrogen abstraction could account for the



ene products. In order to assess the importance of such a pathway, we carried out the pyrolysis of 1 in the presence of a large excess of methylene chloride. If silyl radicals are produced in the pyrolysis, rapid chlorine abstraction should surpress the hydrogen abstraction[12] and chlorodimethylvinylsilane should appear as the main silicon-containing product of the ene pathway.

We have tested this method for detecting silyl radicals by carrying out the copyrolysis of methylene chloride with allyltrimethylsilane, a known source of silyl radicals.[13] The trimethylsilyl radicals are scavenged in nearly quantitative yield to give trimethylchlorosilane. None of the secondary products usually associated with silyl radicals are produced in the presence of methylene chloride.[14]

When the flash vacuum pyrolysis of 1 is carried out in the presence of an excess of methylene chloride, the product distribution is not affected (experiment 4). Because of the increased pressure differential across the reaction zone, the residence time of 1 is decreased, resulting in a correspondingly lower percent decomposition. The relative amounts of isobutene and 3 remain nearly constant (cf. experiment 2), and the ene/dimer ratio is consistent with the flow rate. No chlorodimethylvinylsilane is detected in the reaction mixture. Silyl radicals are thus eliminated as precursors to the isobutene and 3, products of the silene 4. In light of these results, the most reasonable alternative is an intramolecular ene reaction of 1,1-dimethyl-2-neopentylsilene.

In a large number of bimolecular reactions between silenes and organic systems such as propene,[15] isoprene,[16] and acetone,[17] acyclic products containing the exchanged fragments of both reaction partners are found. For the most part, these reactions have been described in terms of the sequence: cycloaddition and ring opening to biradicals, followed by hydrogen atom migration. However, it is conceivable that these reactions proceed by an *intermolecular* concerted pericyclic process. Experiments to explore this possibility are currently in progress in our laboratories.

Acknowledgment is made to the Robert A. Welch Foundation, the Research Corp., and the North Texas State University Faculty Research Fund for their support of this work.

Registry No. *endo*-1, 74107-88-3; *exo*-1, 74107-87-2; *cis*-2, 62518-77-8; *trans*-2, 62518-76-7; 3, 18243-27-1; 4, 79991-59-6; isobutene, 115-11-7; cyclopentadiene, 542-92-7.

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(13) Davidson, I. M. T.; Wood, I. T. *J. Organomet. Chem.* **1980**, *202*, C65.
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Condensation of Propiolic Esters with Olefins Catalyzed by the $C_5H_5Fe(CO)_2$ Cation

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Summary: Methyl propiolate or tetrolate condense with a number of olefins in a reaction catalyzed by either η^5-$C_5H_5Fe(CO)_2$(isobutylene)BF_4 or η^5-$C_5H_5Fe(CO)_2$(THF)-BF_4 to give 1,3-dienes, cyclobutenes, and 5,6-dihydro-2-pyrones.

The $C_5H_5Fe(CO)_2$ cation (Fp^+) is known to activate olefins in $Fp(\eta^2\text{-olefin})^+$ x^- complexes toward addition by

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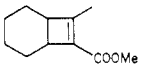
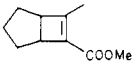
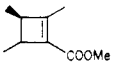
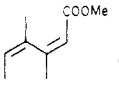
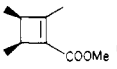
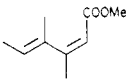
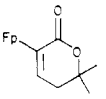
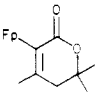
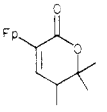
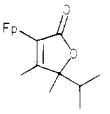
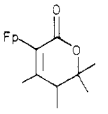
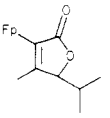
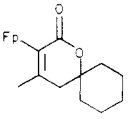
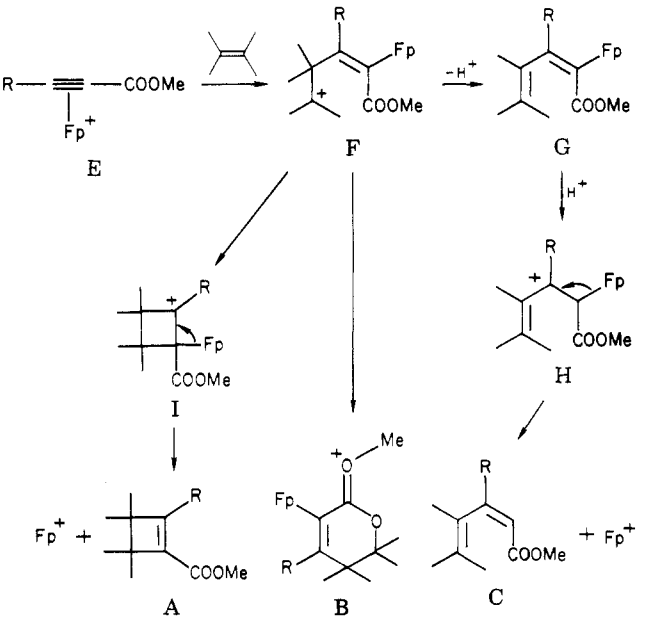
Table I. Reactions of Alkenes and Acetylenic Esters with Fp^+

alkene	ester	$FpL^+BF_4^-$ (mol %)	products (yield)
	2	4 (10)[a]	 (46)
	2	3 (10)[a]	5 (53)
	2	4 (50)[a]	 (32)
			6
	2	4 (20)[a]	 (22)  (21)
			7 8
	2	4 (20)[a]	 (17)  (16)
			9 10
	1	3 (100)[b]	 (33)
			11
	2	3 (100)[b]	 (53)
			12
	1	3 (100)[b]	 (23)  (5)
			13 14
	2	2 (100)[b]	 (33)  (16)
			15 16
	2	3 (100)[b]	 (66)
			17

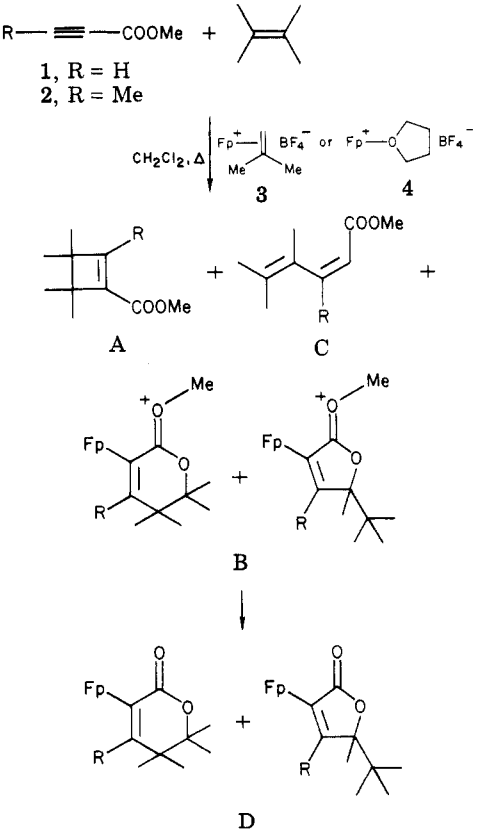
[a] Reaction time, 24 h. [b] Reaction time, 5 h.

carbon[1] and heteroatomic nucleophiles,[2] and we have earlier applied this chemistry in metal-assisted Michael reactions,[3] enolate vinylations[4] and β-lactam synthesis.[5] Similar activation of acetylenic ligands is less extensively explored, but these too have been shown to be effective substrates for nucleophilic attack in Fp(η^2-acetylene) cations.[6] We now find that Fp^+ may function as a unique *catalyst* for cycloaddition and ene[7] type reactions involving

Scheme I



the cocondensation of acetylenic esters and olefins. The overall transformation is given by eq 1, and experimental



(1)

results, obtained with methyl propiolate **1** or methyl tetrolate **2** and a number of alkenes, using Fp(isobutylene)[8] or Fp(tetrahydrofuran) tetrafluoroborate[9] salts as a source

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(9) Reger, D. L.; Coleman, C. *J. Organomet. Chem.* **1977**, *131*, 153. A more convenient and less expensive method for making this compound than the method used in the above references (FpX + $AgBF_4$ in THF) consists in simply heating complex **3** in THF–CH_2Cl_2 solution for 3.5 h and filtering off the product **4** (79% yield).

of the Fp cation, are summarized in Table I.

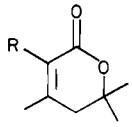
In general a mixture of acetylenic ester, complex **3** or **4**, and the olefin, dissolved in methylene chloride, was heated at reflux for several hours (see Table I). The solution was cooled and concentrated under reduced pressure, and ether was added to precipitate the salt B. This was collected and washed thoroughly with ether. Treatment of these with sodium iodide in acetone solution at 25 °C for 1–2 h gave the lactone products, which were purified by column chromatography on neutral, activity IV alumina, eluting with 10% ether–hexane followed by 70% ether–hexane. The ether-soluble products were concentrated in vacuo and Kugelrohr distilled. Separation of mixtures of products and determination of yields was achieved by gas chromatography.[10,11]

Several features of the reaction are noteworthy with respect to its mechanism and synthetic scope. The formation of cyclobutene A and diene C products is catalytic with respect to complexes **3** or **4**, but it can be shown in a separate experiment that the lactone salts B do not promote the conversion of acetylene and olefin to A and C. Both the dienes **8** and **10** and cyclobutenes **7** and **9** are formed stereospecifically from *cis*- and *trans*-2-butene,[12] consistent with, but not requiring, a concerted mechanism for their formation.[13] Futhermore, the structures of the product olefins **8** and **10** are such as to exclude their formation from cyclobutenes **7** and **9** by a thermal or metal-catalyzed electrocyclic reaction. Finally, the course of the reaction is strongly dependent on the structure of the olefin reactant; 1,2-disubstituted cyclic and acyclic alkenes yield cyclobutenes and 1,3-dienes in addition to some lactone salts, while 1,1-disubstituted or trisubstituted alkenes gave only the latter products. Monosubstituted olefins yield principally their Fp complexes.

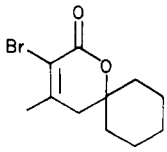
The mechanism shown in Scheme I plausibly accounts for these experimental results.

Initial transfer of Fp^+ from **3** or **4** to the acetylenic ester gives the highly reactive complex E. We have already provided evidence for the formation of such a species in exchange reactions with **3**[6] and for its reaction with nucleophiles competitive[6,14] with rearrangement to a cationic vinylidene complex.[15] The cation F, formed by the reaction of the acetylene complex with an olefin, may be expected to undergo several competing reactions. Proton transfer (F → G → H → C) results in the formation of diene and regeneration of Fp^+ catalyst. Although this sequence bears some resemblance to the Lewis acid promoted ene reactions of propiolic esters with olefins,[7,16] an important distinction lies in the formation of 1,4-dienes in these latter reactions, apparently due to proton loss through a six-membered dipolar transition state or intermediate.[16] Significantly, such a transition state is not available to F.[17] The stereochemistry assigned to F follows from anticipated trans addition[1] of olefin to the acetylene complex E and allows for the observed formation of both δ- and γ-lactone salts B, by either direct closure of F or by carbonium ion rearrangement prior to closure. These latter complexes, unlike intermediate G, should be resistant to proton-initiated demetalation owing to their charge, and hence the formation of B irreversibly consumes the catalyst Fp^+. Alternatively, cyclization of F may proceed through the cyclobutyl cation I and thence by elimination of Fp^+ to product A, in a second catalytic cycle. Throughout, the Fp group plays an important role in promoting the cyclization of F to B and I and in the demetalation of G through the stabilization of cationic charge β to it in these substances.[18]

Facile demetalation of **12** is also achieved by treatment with I_2 (CH_2Cl_2, 3 h, 25 °C) or with 48% HBr (Et_2O, 3 h, 25 °C) to give lactones **18a**,[19]**b** (73% and 61% yields, respectively). Similarly, treatment of **17** with Br_2 (CH_2Cl_2, 1 h, 25 °C) gave the spirolactone **19** (55% yield).



18a, R = I
b, R = H



19

Cationic oligomerization and polymerization of alkenes and alkynes by transition-metal salts is well recognized,[20] and an example of such reactions by a discrete organometallic complex dication has recently been given.[21] We had earlier reported the catalytic dimerization of phenylacetylene to give 2-phenylnaphthalene in the presence of **3**.[14] The reactions reported here represent the first examples of carbon–carbon bond formation catalyzed by Fp^+, involving a mixed acetylene–olefin system. Further experiments designed to examine the generality of the reaction and its synthetic applications are in progress.

Acknowledgment. This research was supported by a grant from the National Science Foundation (No. CHE-7816863) which is gratefully acknowledged.

Registry No. **1**, 922-67-8; **2**, 23326-27-4; **3**, 41707-16-8; **4**, 63313-71-3; **5**, 79953-73-4; **6**, 79970-17-5; **7**, 73588-18-8; **8**, 79953-74-5; **9**, 79953-75-6; **10**, 79953-76-7; **11**, 69627-24-3; **12**, 79972-23-9; **13**, 79972-24-0; **14**, 79972-25-1; **15**, 79972-26-2; **16**, 79972-27-3; **17**, 79972-28-4; **18a**, 79953-77-8; **19**, 79953-78-9; cyclohexene, 110-83-8; cyclopentene, 142-29-0; *trans*-2-butene, 624-64-6; *cis*-2-butene, 590-18-1; isobutylene, 115-11-7; 2-methyl-2-butene, 513-35-9; methylenecyclohexane, 1192-37-6; **18b**, 6970-56-5.

(10) Final purification and analysis was carried out by GLC on a 6 ft × $^1/_4$ in. DEGS on chromosorb W column at 85 °C.

(11) All new products have been fully characterized by IR and ^1H NMR spectra and by elemental or ^{13}C NMR spectral analysis.

(12) Assignments of **7** and **9** were made by decoupling the ring protons from the methyl proton resonances: $J_{H\text{-}3,H\text{-}4}(7) = 1.5$ Hz, $J_{H\text{-}3,H\text{-}4}(9) = 4.6$ Hz. The stereochemistry of the C(2),C(3) double bond in **8** and **10** is consistent with the chemical shifts observed: for C(3) methyl groups, **8**, **10** ($CDCl_3$) δ 1.90; for *cis*-crotonic ester, δ 2.14; for *trans*-crotonic ester, δ 1.88. The stereochemistry of the C(4),C(5) double bond in **8** and **10** is in accord with methyl group carbon resonances in their ^{13}C spectra: **8** ($CDCl_3$) δ 23.9, 21.8, 14.1; **10** ($CDCl_3$) δ 25.5, 15.1, 13.4.

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(16) Snider, B. B.; Roush, D. M.; Rodini, D. J.; Gonzalez, D.; Spindell, D. *J. Org. Chem.* **1980**, *45*, 2773.

(17) The stereospecific formation of dienes **8** and **10** precludes the possibility that nonconjugated diene is first formed and subsequently isomerized to a conjugated diene.

(18) These interactions are evident in the unusual chemical stability of lactones B, which are only partially hydrolyzed after being stirred in contact with aqueous bicarbonate solutions for several hours. The neutral lactones, derived from B by iodide treatment, also show the effects of Fp group interactions with electron-defficient centers in their unusually low lactone carbonyl frequencies: for **13** and **15**, 1670 cm^{-1}; for **14** and **16**, 1710 cm^{-1}.

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