monium sulfate precipitate was dissolved in 10 mL of the 0.1 M phosphate, pH 7.6/glycerol/DTE/EDTA buffer and dialyzed overnight at 4 °C against four to five changes of the same buffer. The dialysate supplemented with 0.1 M $MgCl_2$ was used as the source of enzyme in the incubations at 26 °C. For the run in $[^{18}O]$water, the dialysate was first lyophilized, dissolved in 1 mL of $[^{18}O]$water, relyophilized, and then redissolved in $[^{18}O]$-water.

(7) Obtained from Mound Laboratory, Miamisburg, Ohio.

(8) Mass spectra were obtained at 50 eV using a Hitachi Perkin-Elmer RMU-6D mass spectrometer. Regions of interest were repetitively scanned at slow speed and the areas of the resulting peaks determined by cutting and weighing. Isotope enrichments represent the average of several scans and are corrected by comparison with spectra of unlabeled substrates.

(9) H. L. Goering, J. N. Eikenberry, and G. S. Koermer, *J. Am. Chem. Soc.*, **93**, 5913 (1971).

(10) The $^3H/^{14}C$ ratio was determined by hydrolyzing a portion of the nerolidyl pyrophosphate mixture with alkaline phosphatase to free $[^3H,^{14}C]$nerolidol, which was converted, as previously described,[4] to the crystalline 10,11-dihydroxynerolidol (mp 72–73 °C) which was then recrystallized to constant activity.

(11) Cf. E. Leistner, R. N. Gupta, and I. D. Spenser, *J. Am. Chem. Soc.*, **95**, 4040 (1973).

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(14) The present experiment measures only *net* scrambling of nerolidyl pyrophosphate released from the isomerase. In the absence of purified enzyme it is not possible to determine the scrambling for a single turnover, nor the number of times FPP and NPP are interconverted at the active site prior to product release. The presence of the cyclase, which converts the NPP to cyclonerodiol pyrophosphate, while not excluding rebinding of free NPP to the isomerase, makes such an event unlikely. Reversal of pathway A would not result in the observed scrambling, since in this mechanism the oxygens attached to P_α remain stereochemically distinct.

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(19) Fellow of the Alfred P. Sloan Foundation, 1978–1980; National Institutes of Health Research Career Development Award, 1978–1983.

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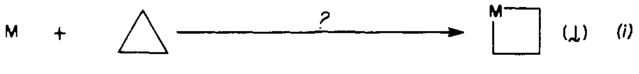
Reactions of Organocyclopropanes and Spirocycles with Metal Atoms

Sir:

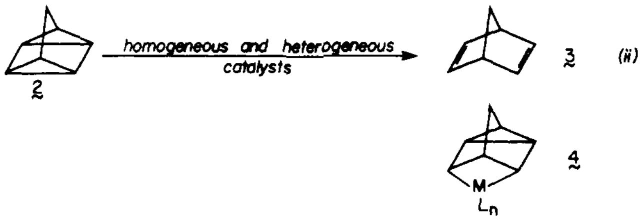
Interest in the reactions of metal *atoms* with organocyclopropanes arises from the possibility of realizing direct metallocyclobutane generation[1] (eq i) and the wealth of chemistry



M = metal atom

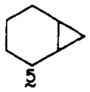
which has been observed between metal *complexes* and organocyclopropanes under homogeneous conditions.[2] We report in this communication an extensive study which precisely delineates the substrate features required to observe metal atom–organocyclopropane reactions. Furthermore, this investigation has also resulted in a new and potentially general metallocene synthesis: the cocondensation of iron atoms with spirocyclic precursors affords entry into a number of novel, difficultly accessible substituted ferrocenes.

The highly strained bis(cyclopropane)quadricyclane (**2**) is thermally robust (half-life 14 h at 140 °C)[3] but is rapidly isomerized to norbornadiene (**3**) by a variety of metal catalysts (eq ii).[3,4] Metallocyclobutanes such as **4** have been postulated as intermediates in this isomerization. We cocondensed **2** with a variety of metal atoms at 77 K over a 0.5–1.0-h period in the type of reactor employed by Skell[5] and Klabunde.[6] The matrix was allowed to warm for 1 h under static vacuum (unless noted) before product analysis. While the data, summarized in Table I, indicate the ability of **2** to undergo reaction, control experiments suggest that little if any **4** is formed.



A comparison of entries 3–5 (Table I) is instructive. Cocondensation of **2** and chromium (entry 3) resulted in the efficient isomerization of **2** to **3**. When chromium alone was evaporated onto the reactor walls (77 K), followed by deposition of **2** (entry 4), little isomerization was observed. Thus chromium surfaces produced in this fashion do not efficiently isomerize **2**. However, when a cocondensation was conducted as usual but the subsequent 1-h matrix warmup eliminated (entry 5), virtually no isomerization was observed. During the warm-up period, the matrix melts and, if no stable complexes are formed, the metal aggregates. Klabunde has shown that finely dispersed metal particles which have superior catalytic properties are produced under these conditions.[7] Since entry 5 indicates the yield of **3** is dependent upon the contact time of **2** with the metallic residue from the thawed matrix, we conclude that most of the observed isomerization is heterogeneously catalyzed. Similar results were obtained in experiments with iron, in which lower ratios of **2** to metal were employed. Significantly, a preformed iron surface (entry 7) was as active as codeposited iron (entry 6).

Reactions of norcarane (**5**) and the structurally related vinylic and allylic cyclopropanes (**6–8**) with metal atoms (see formulas below) were investigated next. It has been generalized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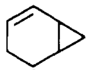
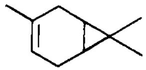
V,Cr,Fe


6
Ti,Cr,Ni,Pd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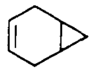
Ti,Cr,Ni,Pd


8
Cr

that unless the organic reactant has nonbonding or π electrons, metal atom aggregation will be rapid at 77 K.[6] Thus the olefinic groups in **6–8** might be expected to promote reaction by initially binding the metal. However, when reacted as described for **2**, **5–8** were recovered in near-quantitative yields; no isomers could be detected by GLC or ^1H NMR, even in the reactor residue. Since any metallocyclobutane should give subsequent reactions (isomerization, polymerization) upon warming the matrix,[1] we conclude that no carbon–carbon bond insertion occurs.

Although a phenyl substituent might be expected to facilitate cyclopropane ring rupture, cocondensation of chromium atoms (2.3 mmol) with cyclopropylbenzene (**9**, 69 mmol) yielded only the bis(arene) complex **10** (eq iii, 1.0 mmol; 45% based upon chromium).[8] Reactions were also conducted with Ni and V and **9**. In no case was allylbenzene, methylstyrene, or styrene detected.

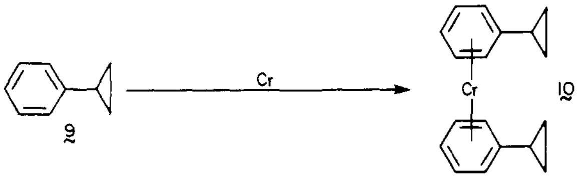


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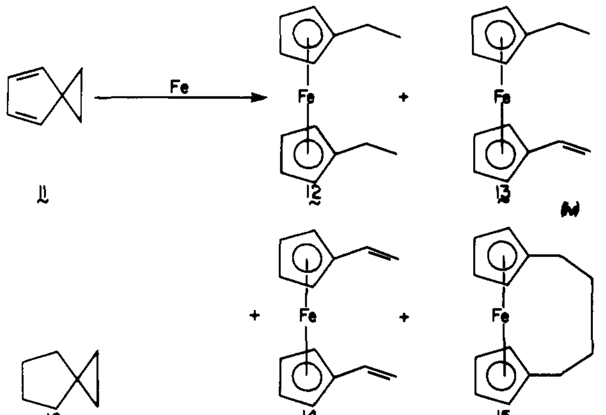
Table I. Quadricyclane (**2**) Reactions

entry	metal and conditions[a]	mmol **2**: mmol metal[b]	recovered **2**,[c] %	yield **3**[c] %	dimer + polymer,[c,d] %	turnover per metal[e]
1	Ti cocondensation	185	88	8	1	16
2	Ti cocondensation	13	82	15	1	2
3	Cr cocondensation	41	25	70	1	29
4	Cr surface	15	97	3	0	0.4
5	Cr cocondensation[f]	13	98	2	1	0.4
6	Fe cocondensation	7.4	0	61	1	5
7	Fe surface	4.7	0	79	1	4
8	Fe cocondensation[f]	5.9	77	18	2	1
9	V cocondensation	17	18	71	4	13
10	Mo cocondensation	56	96	2	1	2
11	Co cocondensation	4.2	0	47	27	3
12	Ni cocondensation	22	20	44	25	15

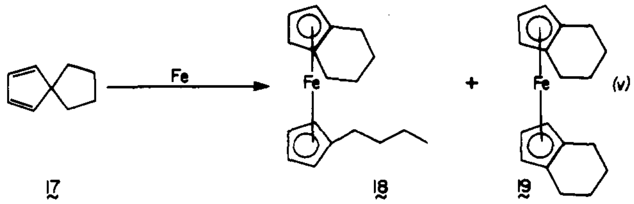
[a] See also text. [b] A titrimetrically determined correction factor is used to calculate the amount of evaporated metal reaching the reaction zone. Reaction scale: 11-22 mmol of **2**. [c] Yields are based upon **2** and represent isolated materials. [d] Material of the formula $(C_7H_8)_n$ ($n \geq 2$) obtained by extraction of the reactor residue after pumping off **2** and **3**. [e] mmol of **2** reacted/mmol of metal. [f] One-hour warm-up omitted; volatiles (**2**, **3**) pumped directly into trap as matrix warms.

The doubly vinylic cyclopropane, spiro[2.4]hepta-4,6-diene (**11**),[9] was prepared as an optimal substrate for reactions with metal atoms. Gratifyingly, this ligand underwent reaction with a variety of metals. Cocondensation of **11** (100 mmol) with iron atoms (5.7 mmol) yielded the substituted ferrocenes **12–15** (44% yield based upon iron) in a 14:64:6:17 ratio (eq iv).[10]



11 12 13 14 15 16

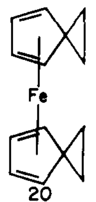
Subsequent experiments provided information on the means by which the cyclopropane ring in **11** is cleaved. The saturated homolog, spiro[2.4]heptane (**16**), failed to react with iron atoms. Hence, the diene functionality in **11** must play an important role in cyclopropane activation and/or iron binding. The less strained spiro[4.4]nona-1,3-diene (**17**)[9] did react upon cocondensation with iron, although in lower (5–20%) yield; the major products formed were **18** and **19** (eq v; variable ratios).[12] No 1,1′-dibutylferrocene or 1-butyl-1′-butenylferrocenes were produced,[12] although minor amounts of other products were detected. Thus the driving force for ring rupture of **11** is apparently coupled to the formation of an aromatic cyclopentadienyl ring and the formal oxidation of iron.



17 18 19

The bis(diene) complex **20** represents a possible precursor to **12–15**. Hence attempts were made to intercept **11** as a ligand on iron prior to ring opening. Complexes of the formula (diene)FeL_3 are commonly available by adding phosphites to diene-iron matrices, or by cocondensing iron with diene-phosphite mixtures.[14] However, even when a 4:1 mixture of $P(OCH_3)_3$: **11** was cocondensed with iron, only ferrocenes **12–15** were formed. These results suggest that cyclopropane ring opening occurs shortly after or synchronously with the coordination of **11** to iron. The reaction of **11** with $Fe_2(CO)_9$ also yields exclusively ring-opened products.[15]

Ferrocenes **12–15** can be rationalized as arising from the biradical **21**, although intermediates with iron-carbon σ bonds cannot be ruled out.[16] An intramolecular transfer of a quasi-benzylic hydrogen of **21** accounts for the formation of the major product **13**. **12** would be formed by H· abstraction from the matrix, and **14** by loss of two H·. The ferrocenophane **15** represents an internal coupling product. A cyclization-prone biradical intermediate can similarly account for the formation of **18** and **19** from **17**.



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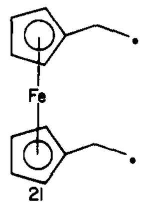

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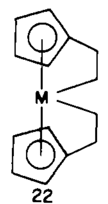

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In summary, this study has established that metal atoms will reaggregate at a much faster rate than they undergo reaction with organocyclopropanes unless a functional group is present that the metal atom can strongly interact with. However, the isolation of **10** indicates that strong binding is not in itself sufficient to achieve cyclopropane ring opening; the three-membered ring must be provided with additional activation as in **11**. While metallocyclobutane formation apparently does not occur when **11** is reacted with iron atoms, other metals might afford cyclic products such as **22**. Indeed, preparative extension of these reactions (eq iv, v) to other spirocycles and metals should provide direct entry into otherwise difficultly accessible metallocenes. Finally, our establishment of surface-catalyzed quadricyclane isomerization indicates that caution must be exercised in interpreting the results of metal atom-organic molecule cocondensations in which only organic (as opposed to organometallic) products are formed. Careful controls, and optimally spectroscopic experiments, must be done to ensure that the observed chemistry arises from metal *atoms* and not metal *surfaces*.[17]

Acknowledgment. We thank the National Science Foundation (CHE76-11247) and the Jane Coffin Childs Memorial Fund for Medical Research for support of this work. The

200-MHz NMR spectrometer used in this study was obtained via a NSF instrument grant (CHE76-05925).

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(8) ^{1}H NMR (δ, C_6D_6, $(CH_3)_4Si$ standard): 4.23 (5 H, s, br), 1.48 (1 H, m), 0.55 (2 H, m). ^{13}C NMR (C_6D_6, $(CH_3)_4Si$ standard): 94.8, 75.3, 75.1, 74.9 (arene carbons), 15.4, 8.3 (cyclopropane carbons) ppm. Mass spectrum: *m/e* 288 (18), 170 (47), 142 (14), 118 (100), 117 (100), 103 (19). Anal. of $B(C_6H_5)_4^-$ salt ($C_{42}H_{40}CrB$). Calcd: C, 83.03; H, 6.64; Cr, 8.56. Found: C, 82.73; H, 6.75; Cr, 8.32.

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(10) After separation by preparative GLC, products were fully characterized by ^{1}H NMR, ^{13}C NMR, and mass spectroscopy; **12** and **15** are known compounds.[11] **13** and **14** were hydrogenated (PtO_2, EtOAc, 48 psi H_2, 2 h) to **12**, which was identical with an authentic sample. Data will be reported in our full paper.

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(12) Typical reaction quantities: 35.0 mmol of **17**; 1.36 mmol of Fe; 0.173 mmol of products, which were separated by preparative GLC. **19** is a known compound[13] and was identified by comparison to an authentic sample; the 200-MHz ^{1}H NMR and 50.32-MHz ^{13}C NMR spectra of **18**, which is a new compound, were virtual superpositions of those of **19** and 1,1′-dibutylferrocene.[11b] The latter could not be detected in the reaction mixture, either before or after hydrogenation.[10]

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(17) For additional comments, see Gladysz, J. A.; Fulcher, J. G.; Lee, S. J.; Bocarsly, A. B.; *Tetrahedron Lett.* **1977**, 3421.

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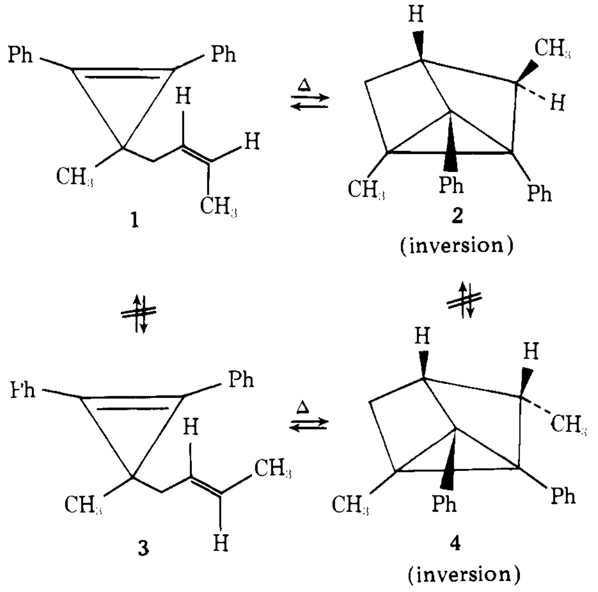
On the Stereochemical Course of the Thermal and Photosensitized Intramolecular [2 + 2] Cycloaddition Reaction of Allyl-Substituted Cyclopropenes[1]

Sir:

Cycloaddition of two olefins and its reverse, cycloreversion or the cleavage of cyclobutane, have been the object of extensive theoretical[2] and experimental studies.[3] Thermal [2 + 2] cycloaddition reactions of olefins can be symmetry allowed and therefore concerted if the $[{}_\pi 2_s + {}_\pi 2_a]$ combination mode is followed. To our knowledge, no authenticated examples of this phenomenon have been reported to date with simple π systems.[4,5] Presumably this is because steric hindrance and angle strain factors generally develop to rather prohibitive levels as the two π bonds attempt to attain the requisite orthogonality. Related studies dealing with the pyrolysis of stereochemically labeled alkylcyclobutanes have disclosed that antarafacial motion by at least one of the developing olefinic moieties is not readily achieved.[6] As a result, little stereoselectivity has been observed. In this communication we wish to describe the stereochemical course of the thermal and photosensitized intramolecular [2 + 2] cycloaddition reactions of a number of allyl-substituted cyclopropenes. Although the results obtained are compatible with orbital symmetry predictions,[2] the cycloaddition reactions actually proceed via a diradical intermediate.

Thermolysis of (*Z*)-1,2-diphenyl-3-methyl-3-(2-butenyl)cyclopropene (**1**) at 190 °C for 48 h produced an equilibrium mixture of recovered starting material (55%) and *exo*-3,6-dimethyl-1,2-diphenyltricyclo[2.2.0.0^{2,6}]hexane (**2**) (45%). The same distribution of products was obtained by heating tricyclohexane **2** at 190 °C for 48 h. The thermal cycloaddition reaction of the isomeric *E*-substituted cyclopropene **3** was also investigated.[7] Heating a sample of cyclopropene **3** under similar conditions afforded an equilibrium mixture of recovered starting material (80%) and *endo*-tricyclohexane **4** (20%). Appropriate control experiments established that no cis–trans isomerization of either the starting materials or the products was operative under the reaction conditions.



The thermal chemistry of the closely related (*Z*)- (**5**) and (*E*)-1,3-diphenyl-2-methyl-3-(2-butenyl)cyclopropenes (**6**) were also studied so as to provide additional documentation for the stereochemical course of the cycloaddition reaction. Thermolysis of cyclopropene **5** at 175 °C for 12 h afforded a mixture of *exo*-tricyclohexane **7** (16%) and cyclopropene **8** (11%).[8] Subjection of **6** to similar thermolysis conditions produced a 2:1 mixture of *endo*-tricyclohexane **9** and cyclopropene **8**. The structures of the *endo*- and *exo*-methyl-substituted tricyclohexanes were easily assigned on the basis of their characteristic 270-MHz NMR spectra. The absence of coupling between H_3 and H_4 with tricyclohexanes **2** and **7** fixes the C_3-methyl group in the exo position. This is to be expected since molecular models show that the dihedral angle for this set of protons is ~90°. Spin-decoupling experiments indicate that protons H_3 and H_4 in the endo-substituted series (**4** and **9**) are coupled by 4.5 Hz.[9]

The striking feature of these results is that the intramolecular thermal cycloaddition reaction proceeds with total inversion of stereochemistry about the olefinic π bond. A mechanism which is consonant with all the available data is

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