Experimental Evidence for Orbital Symmetry Control of Stereochemistry in Some (Methylenecyclopropane)iron-Carbonyl Reactions

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Abstract: The reactions of 2-phenylmethylenecyclopropane (1) and 2,2-diphenylmethylenecyclopropane (7) with a variety of iron-carbonyl reagents are presented. The stereochemistry of ring opening of 1 to (phenyltrimethylenemethane)iron tricarbonyl is elucidated by stereospecific deuterium labeling. The deuterium labeling also allows information to be gained about the conversion of I to ((E)-1-phenylbutadiene) iron tricarbonyl. An iron-tetracarbonyl complex obtained from reaction of 7 with $Fe_2(CO)_{9}$ is identified by X-ray crystallography and shown to be a plausible intermediate in the formation of (1,1-diphenyltrimethylenemethane)iron tricarbonyl. A general mechanism is presented for the reactions studied in this work. It is shown to be consistent with stereochemical predictions derived from consideration of frontier molecular orbital symmetry and to provide an alternative explanation for some previously studied methylenecyclopropane/Fe₂(CO)₉ reactions.

There have been numerous attempts to employ qualitative symmetry-based quantum mechanical theories¹ to the analysis of metal-assisted concerted organic reactions.²⁻⁷ Unfortunately, experimental tests of the predictions arising from these theories have been scarce, in part because of the difficulty of finding a transition-metal-promoted pericyclic reaction whose stereochemistry was both theoretically predictable and experimentally determinable. The main purpose of this work is to describe what we believe to be the first example of such a reaction.

The early experimental work in this field concentrated on the prediction, common to most of the theories, that certain thermally forbidden¹ pericyclic reactions might become allowed if they occurred within the coordination sphere of an appropriate transition metal. The dramatic catalysis of the quadricyclane-norbornadiene conversion by various Rh(I) complexes⁸ appeared to be an example of such a process until it was shown to proceed in a stepwise, nonpericyclic manner.^{9,10} Later studies turned to investigation of reaction stereochemistries, particularly in the metal-catalyzed ring opening of bicyclo[1.1.0]butane derivatives,^{10,11} but here again further investigation showed that the two C-C bonds of the substrate were breaking in a nonconcerted manner.10,12

One of the few metal-promoted transformations which still appears to be a true pericyclic process is the ring opening of a set of strained (cyclobutene)iron-tetracarbonyl complexes reported by Pettit and co-workers (see eq 1).¹³ Their proposal of a reversible loss of carbon monoxide from the initial Fe(CO)₄ complex, followed by an irreversible ring opening, was strongly supported by the observation that added carbon monoxide or olefins de-

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creased the rate of reaction.¹³ It is the second step which appears to be a true pericyclic (in this case electrocyclic) process. Unfortunately it is not possible to determine the influence of an Fe(CO)₃ unit on the stereochemistry of a cyclobutene ring opening from this experiment. The prohibitive strain associated with the incorporation of a trans double bond in a six-membered ring precludes the isolation of any products which might have come from conrotatory ring opening or from the disrotatory mode which bends the breaking σ bond away from the metal.

The ring opening of 2-phenylmethylenecyclopropane (1) by



Fe₂CO)₉¹⁴ would appear to be a better source of stereochemical information, provided that it could be shown to be a pericyclic process analogous to Pettit's reaction.¹³ At the inception of this study there was little support for such an analogy in the literature. Billups and co-workers¹⁵ had proposed a zwitterionic mechanism for the ring opening of 2,2-dimethylallylidenecyclopropane by Fe₂(CO)₉ (Figure 1).

Whitesides et al.^{16,17} found that the iron-tetracarbonyl complexes of cis or trans Feist's esters (dimethyl methylenecyclopropane-2,3-dicarboxylate) gave (butadiene)iron-tricarbonyl complexes and a small amount of a dinuclear complex upon heating or treatment with excess Fe₂(CO)₉. They proposed a mechanism involving two $Fe(CO)_4$ units (Figure 2).

The work described in this paper leads to the proposal of a new mechanism which seems to be able to encompass the results of Noyori,¹⁴ Billups,¹⁵ and Whitesides¹⁶ as well as the new data obtained in our laboratory.

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Figure 1. Zwitterion mechanism for formation of the trimethylenemethane complex.

Scheme I



Results

Theoretical Studies. In order to compare the expected stereochemistries, for ring opening of (cyclobutene)- and (methylenecyclopropane)iron-carbonyl complexes, we carried out extended Hückel calculations on the prototype reactions shown in Scheme I. The results of these calculations have been reported elsewhere⁷ but can be summarized as follows. Simple symmetry arguments allow one to deduce that, for the cyclobutene complex, the disrotatory ring opening which bends the breaking σ bond toward the metal should be lower in energy than the disrotatory mode which bends the σ bond away from the metal. The situation is exactly reversed for the methylenecyclopropane complex. Now the disrotatory-away mode is predicted to be of lower energy. This prediction is central to our interpretation of the experimental results presented below. Extended Hückel calculations for approximate conrotatory mode reaction coordinates were carried out on the (cyclobutene)- and (methylenecyclopropane)irontricarbonyl complexes. The results placed the conrotation between the two disrotatory modes for the cyclobutene complex and very slightly below the disrotatory-away mode for (methylenecyclopropane)iron tricarbonyl. However since conrotation maintains no symmetry element, its relative favorability is not subject to ready qualitative explanation and is accordingly more model dependent. It seems appropriate, therefore, to place more confidence in the predicted relative favorability of the two disrotatory modes than in the ordering of disrotatory and conrotatory mechanisms.

Reactions with 2-Phenylmethylenecyclopropane (1). Reaction of 1 with $Fe_2(CO)_9$ in benzene for 5 h at room temperature gave (phenyltrimethylenemethane)iron tricarbonyl (2) as previously reported.¹⁴ However under these conditions a considerable amount of unchanged 1 remained. At longer reaction times a new product started to appear. This was identified as ((E)-1-phenylbutadiene) iron tricarbonyl (3) by comparison of its IR and ${}^{1}H$ NMR spectra with those reported¹⁸ for this complex. A control experiment showed that 2 and 3 did not interconvert under the reaction conditions and that some other explanation for the product ratio time dependence was thus required.

When 1 was reacted with iron pentacarbonyl and trimethylamine N-oxide¹⁹ in benzene at room temperature, a rather different result was obtained. Now the trimethylenemethane complex (2)was the exclusive product (within our detection limits) for all reaction times. This result was unexpected since $Fe_2(CO)_0$ and $Fe(CO)_5/(CH_3)_3NO$ are thought to generate $Fe(CO)_4$ as a common reactive intermediate.¹⁹ A control experiment showed that treatment of an equimolar mixture of 2 and 3 with $(CH_3)_3NO$ caused no measurable change in their relative concentration,





Figure 2. Mechanism of Whitesides et al.¹⁶ for the ring opening of Feist's ester Fe(CO)4.

indicating that failure to obtain 3 from reaction of 1 with Fe- $(CO)_5/(CH_3)_3NO$ was not due to selective product destruction by the $(CH_3)_3NO$. In a second experiment 1 and (trimethylamine)iron tetracarbonyl²⁰ were found not to react at an appreciable rate in benzene at room temperature, showing that (C- $H_{3}_{3}NFe(CO)_{4}$ could not be the reactive intermediate in the $Fe(CO)_5/(CH_3)_3NO$ system.

These data suggest two general hypotheses: either the formation of the butadiene is a special feature of the $Fe_2(CO)_9$ reaction or failure to form the butadiene is a special feature of reactions with (CH₃)₃NO. Two experiments were run which support the second hypothesis and rule out the first. Addition of (CH₃)₃NO to the reaction involving $1 + Fe_2(CO)_9$ decreased the 3:2 ratio at the end of the reaction from 0.77:1 to 0.08:1. One might have expected that if the butadiene complex was formed from a dinuclear reactive intermediate such as $Fe_2(CO)_8$, which might be accessible to $Fe_2(CO)_9$ but not $Fe(CO)_5/(CH_3)_3NO$, then addition of (C- $H_3)_3NO$ would increase the concentration of $Fe_2(CO)_8^{21}$ and increase the 3:2 ratio. The first hypothesis was effectively ruled out by the observation that reaction of 1 with (benzylideneacetone)iron tricarbonyl^{22,23} ((BDA)Fe(CO)₃) afforded both 2 and 3 in a time-dependent ratio.

The results on the reaction of 1 with the various iron-carbonyl sources are summarized in Table I. Possible explanations for the product ratio time dependence and for the effect of (CH₃)₃NO

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Table I. Product Distribution from Reaction of2-Phenylmethylenecyclopropane with VariousIron-Carbonyl Reagents



^a (BDA)Fe(CO)₃ = (benzylideneacetone)iron tricarbonyl.





are presented in the Discussion.

Reactions with cis- and trans-2-Phenylmethylenecyclopropane-3- d_1 . Application of the zwitterion mechanism¹⁵ to the formation of 2 from 1 is shown in Figure 3. The crucial feature of this mechanism, rendering it subject to experimental test, is that the zwitterion intermediate 6 possesses a plane of symmetry which bisects the H-C3-H angle. Involvement of intermediate 6 consequently implies that the two hydrogens attached to C3 must become temporarily equivalent by symmetry and that one would therefore expect identical label distributions in the trimethylenemethane complexes from cis-2-phenylmethylenecyclopropane-3-d (5).

cis- and trans-2-phenylmethylenecyclopropane-3-d were synthesized in order to test this hypothesis. Attempts to modify the synthesis of 2-phenylmethylenecyclopropane²⁴ to allow preparation of the deuterated analogues were unsuccessful because treatment of the 1-chloro-1-methyl-2-phenylcyclopropane-3-d intermediate²⁴ with potassium tert-butoxide produced 2-phenylmethylenecyclopropane-3-d in which the label had completely equilibrated between cis and trans sites. The synthetic route which was finally successful is shown in Figure 4.

Following our completion of these syntheses, a similar sequence of reactions involving dichlorocarbene cyclopropanation was reported,²⁵ although this work used unlabeled substrates and only carried the sequence as far as the β -haloalcohol.

Reaction of 4 and 5 with $Fe_2(CO)_9$ in benzene produced phenyltrimethylenemethane complexes in which the label locations were clearly different, as judged by comparison of their ¹H NMR spectra (Figure 6). This result allowed unambiguous rejection of the mechanism shown in Figure 3.

In order to determine the location of the labels in the deuterated phenyltrimethylenemethane complexes, it was necessary to assign the resonances in the ¹H NMR spectrum of **2**. An assignment had been reported, ²⁶ but it seemed appropriate to confirm it, since



Figure 4. Synthetic route to cis- and trans-2-phenylmethylenecyclopropane-3-d. (4, $R_1 = D$, $R_2 = H$; 5, $R_1 = H$, $R_2 = D$): (a) *i*-Bu₂AlH; (b) (R_2)₂O; (c) PhHgCBr₃; (d) *t*-BuLi; (e) CO₂; (f) H₃O⁺; (g) CH₂N₂; (h) LiAlH₄; (i) CH₃SO₂Cl/Et₃N.





Figure 5. Percent nuclear Overhauser enhancement.

determination of the stereochemistry of ring opening rested on this information. Confirmation was achieved through a combination of ¹³C¹H} and proton-proton nuclear Overhauser enhancement (NOE) techniques. The off-resonance-decoupled ¹³C NMR spectrum of 2 showed, in addition to the phenyl resonances and the singlet resonance for the central carbon of the trimethylenemethane, two triplet resonances at 51.1 and 54.4 ppm and a doublet at 79.2 ppm (downfield from Me₄Si, C₆D₆ solvent). The doublet resonance could be assigned to the phenyl-bearing carbon since it alone bore a single proton. The ¹H NMR spectrum (C_6D_6) showed resonances at δ 1.4 (s + d, 2), 1.9 (d, J = 2.5 Hz, 1), 2.6 (d, J = 4.5 Hz, 1), 3.9 (d, J = 2.5 Hz, 1), 7.0 (m, 5). Irradiation of the sample at a frequency corresponding to the δ 3.9 resonance in the ¹H NMR spectrum caused the doublet resonance at 79.2 ppm in the ¹³C NMR spectrum to collapse to a singlet, thereby assigning the δ 3.9 resonance to the proton on the phenyl-bearing carbon. This was then the starting point for the NOE experiment, the results of which are summarized in Figure 5.

NOE was observed for pairs of hydrogens which were geminally related or "U" related on the trimethylenemethane skeleton. The results allowed an unambiguous assignment of each resonance (Figure 6). The final assignments were in accord with those suggested by Ehrlich and Emerson.²⁶

Identification of the resonances in the ¹H NMR spectrum of 2 allowed determination of the label location in the trimethylenemethane complexes derived from 4 and 5 (Figure 6). This, in turn, defined the stereochemistry of the ring opening as the specific disrotatory mode shown in eq 2. Integration of the

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Figure 6. Assignment of labeled trimethylenemethane complexes.



Figure 7. Synthetic routes to ((E)-1-phenylbutadiene-2-d)iron tricarbonyl and ((E)-1-phenylbutadiene-3-d)iron tricarbonyl: (a) LiAlD₄; (b) MnO₂; (c) Ph₃P=CH₂; (d) Fe₂(CO)₉; (e) *i*-Bu₂alH; (f) CH₃Li; (g) CH₃CHO; (h) POCl₃/py.

NMR spectra showed that the ring opening was stereospecific, within experimental error.²⁷

$$\begin{array}{c} Ph & H_{c} \\ \hline Ph & H_{t} \end{array} & Fe_{2}(CO)_{e} \\ \hline Ph & H_{t} \end{array} & H_{t} & Fe_{2}(CO)_{e} \end{array}$$

Identical results were obtained when $Fe(CO)_5/(CH_3)_3NO$ or (BDA)Fe(CO)₃ were used in place of $Fe_2(CO)_9$.

The formation of ((E)-1-phenylbutadiene)iron tricarbonyl, **3**, from 2-phenylmethylenecyclopropane appears to require cleavage of the C1–C2 bond and migration (not necessarily direct) of a hydrogen from C3 to C1. Since C3 had already been stereospecifically labeled for the work described above, it was a relatively simple task to determine which of the two hydrogens on C3 underwent the migration.

(E)-1-Phenylbutadiene-2-d and (E)-1-phenylbutadiene-3-d were synthesized and converted to their iron-tricarbonyl complexes as shown in Figure 7.

Comparison of the butadiene complexes formed from cis- and trans-2-phenylmethylenecyclopropane-3-d and Fe₂(CO)₉ with the independently prepared samples showed that exclusively the cis hydrogen on C3 had migrated. There was also some evidence of an isotope effect on the product distribution when the cis-deuterated phenylmethylenecyclopropane was used. The results are summarized in Figure 8.



Figure 8. Summary of products from labeled and unlabeled 2-phenylmethylenecyclopropanes with $Fe_2(CO)_9$. The product ratio from *cis*-2phenylmethylenecyclopropane-3-d would be 75% trimethylenemethane complex and 25% butadiene complex if corrected for incomplete deuteration.



Figure 9. Computer-generated perspective drawing of (2,2-diphenylmethylenecyclopropane)iron tetracarbonyl. Hydrogens are omitted for clarity.

The small difference in product distribution between reactions run with unlabeled 2-phenylmethylenecyclopropane and with *trans*-2-phenylmethylenecyclopropane-3-d may be indicative of a secondary isotope effect although we are not confident that the difference is outside of experimental error limits.

Reactions with 2,2-Diphenylmethylenecyclopropane. Reaction of 2,2-diphenylmethylenecyclopropane (7) with $Fe_2(CO)_9$ in benzene produced two main products. One was the known¹⁴ (1,1-diphenyltrimethylenemethane)iron tricarbonyl (8). The other was tentatively identified as (2,2-diphenylmethylenecyclopropane)iron tetracarbonyl (9) on the basis of its ¹H NMR, IR, and chemical ionization mass spectra. This identification was confirmed by a single-crystal X-ray diffraction analysis. Figure 9 shows a computer-generated perspective drawing of the final X-ray structure for (2,2-diphenylmethylenecyclopropane)iron tetracarbonyl (9). In general, all bond distances and angles agree well with expected values and no abnormally short intermolecular contacts are present in the crystal. Details of the X-ray study are given in the Experimental Section.

(2,2-Diphenylmethylenecyclopropane)iron tetracarbonyl (9) did not give 8 on standing at room temperature in benzene. Warming to 40 °C resulted in partial decomposition to 7 and Fe₃(CO)₁₂, still with no evidence for formation of 8. Reaction of 9 with Fe₂(CO)₉ in benzene at room temperature did result in the formation of 8, however. The ring opening of 9 to 8 could also be induced by careful treatment with a dilute solution of $(CH_3)_3NO$ in benzene, at or below room temperature.



Discussion

The data acquired in this work, when combined with previous observations,¹⁴⁻¹⁶ lead to a number of critical questions.

(1) What is the explanation for the time dependence of the product ratio, 2:3, observed in the reaction of 2-phenyl-methylenecyclopropane with $Fe_2(CO)_9$ or $(BDA)Fe(CO)_3$?

(2) What is the mechanism by which $(CH_3)_3NO$ suppresses formation of the butadiene complex 3?

(3) Why does the formation of 2 from 1 follow the particular stereochemical pathway elucidated in this study?

(4) Why does formation of 3 from 1 involve selective migration of the hydrogen cis to the phenyl group?

(5) What is the role of the $Fe_2(CO)_9$ in facilitating the conversion of (2,2-diphenylmethylenecyclopropane)iron tetracarbonyl to the corresponding trimethylenemethane complex and the conversion of the Feist's ester iron tetracarbonyls to their respective diene complexes?¹⁶

We believe there is a mechanism which can provide a natural answer to each of these questions. It is illustrated in Figure 10 for 2-phenylmethylenecyclopropane. The experimental observations cited above can be explained as follows.

(1) Runge-Kutta integration of the kinetic scheme depicted in Figure 10 demonstrates that there exist sets of rate constants which will correctly model the time dependence of the product composition. (There are insufficient data to define one particular set of rate constants.)

The qualitative physical picture for the time dependence is as follows. In the early stages of the reaction the ratio of the two (methylenecyclopropane)iron-tetracarbonyl complexes 10 and 11 is approximately equal to the ratio of rate constants $k_1:k_2$ (see Figure 10). It seems reasonable to assume that steric effects will make $k_1 > k_2$ and hence [10] > [11]. If one assumes that all subsequent intermediates have steady-state concentrations, then the product ratio [2]:[3] will reflect, at least qualitatively, the ratio proceeds the ratio [10]:[11] relaxes to a new value which is a complex function of $k_1, k_{-1}, k_2, k_{-2}, k_3, k_{-3}, k_4, k_{-4}$, and [Fe(CO)₅]. The product distribution shows a similar relaxation, providing the observed time dependence.

(2) A plausible role for $(CH_3)_3NO$ is to attack the complexes 10 and 11 and to remove a CO by a mechanism analogous to that proposed¹⁹ for its reaction with Fe(CO)₅. If the rate of CO loss from 10 and 11 becomes much greater than the rate of their interconversion via the methylenecyclopropane and free Fe(CO)₄, then the ratio [10]:[11] remains fixed at its initial value ($\simeq k_1/k_2$), leading, in turn, to a high proportion of 2 in the product throughout the reaction. This behavior can be successfully modeled in the Runge-Kutta intergration by increasing the magnitudes of k_3 and k_4 while leaving all other rate constants at their previous values. The conversion of (2,2-diphenylmethylenecyclopropane)iron tetracarbonyl to the corresponding trimethylenemethane complex upon treatment with (CH₃)₃NO provides strong support for this mode of action of the amine oxide.

(3 and 4) As pointed out earlier, the experimental results obtained with *cis*- and *trans*-2-phenylmethylenecyclopropane-3-d unambiguously define a disrotatory ring opening for the formation of the trimethylenemethane complex. Our previous theoretical analysis⁷ has shown that under such circumstances one would expect the disrotatory mode which bends the breaking σ bond away from the metal to be the more favorable. As can be seen from Figure 10, this prediction helps to explain a number of experimental observations. The iron-tetracarbonyl complex 10 undergoes CO loss and is then transformed to the observed trimethylenemethane complex by the predicted ring opening mode.



Figure 10. Proposed mechanism for the reaction of 2-phenylmethylenecyclopropane with an $Fe(CO)_4$ source. See text for further discussion.





The situation is completely different for complex 11, however. After CO loss, this complex is faced with two unfavorable ringopening modes.

The electronically preferred mode, bending the σ bond away from the metal, causes the phenyl group to rotate inward where it encounters a steric clash with the Fe(CO)₃ unit and with the endo hydrogen on C3. The sterically more comfortable mode in which the C2–C3 σ bond bends down toward the metal is predicted to be electronically disfavored.⁷ Apparently this dilemma is resolved by leaving the C2–C3 bond intact and cleaving the C3–H bond. It will necessarily be the hydrogen cis to the phenyl group which is transferred to the metal and then eventually to C3 of the diene, as observed experimentally (see Scheme II).

(5) In Figure 10 the intermediate (methylenecyclopropane)iron tetracarbonyls 10 and 11 are postulated to lose CO by ligand exchange with $Fe(CO)_4$ rather than by simple unimolecular dissociation. The experiments with (2,2-diphenylmethylenecycloproapne)iron tetracarbonyl, 9, clearly showed that unimolecular CO loss occurred much more slowly than the formation of the trimethylenemethane complex 8 from 7 and $Fe_2(CO)_9$. Addition of $Fe_2(CO)_9$ to 9 did cause formation of the trimethylenemethane complex. Whitesides and Slaven¹⁶ observed





Figure 11. Proposed mechanism for CO abstraction by $Fe(CO)_4$ and for formation of the dinuclear complex.

similar behavior in the formation of butadiene complexes from Feist's ester iron tetracarbonyls and postulated a mechansim involving direct insertion of a second $Fe(CO)_4$ unit into the C1–C2 bond (Figure 2). While it is possible that a similar mechanism operates with 9, it is difficult to explain why the second $Fe(CO)_4$ unit would insert into the C2–C3 bond in this case and why neither C1–C2 nor C2–C3 insertion is observed for uncomplexed methylenecyclopropanes. Our proposal of CO abstraction by ligand exchange with $Fe(CO)_4$ avoids this problem and is strongly supported by the observation that $(CH_3)_3NO$ serves to convert 9 to $8.^{28}$

A plausible intermediate in the proposed CO abstraction by $Fe(CO)_4$ is a dinuclear complex such as **12** (Figure 11). This intermediate could also be the precursor to the dinuclear complex isolated by Whitesides and Slaven¹⁶ (see Figure 2).

As mentioned in 1 above the ratio of [10]:[11] (Figure 10) is a function of the $Fe(CO)_5$ concentration. It follows, then, that if the proposed mechanism is correct, it should be possible to alter the ratio of the products 2 and 3 by changing $[Fe(CO)_5]$. This was found to be true experimentally; thus when 2-phenylmethylenecyclopropane was reacted with $Fe_2(CO)_5$ in $Fe(CO)_5$ solvent 2 was formed, but no 3 could be detected. Since the ratio of 2:3 formed in benzene solution is 1.3:1 at the end of the reaction, it seems unlikely that the drastic change in product distribution with $Fe(CO)_5$ could be explained as a simple solvent polarity effect (in tetrahydrofuran the final product ratio is 1.0:1). Rather, it seems that $Fe(CO)_5$ changes the final product distribution by chemical interaction, as anticipated in the mechanism shown in Figures 10 and 11.

The conversion of the proposed $(\eta^3$ -allyl)iron tricarbonyl hydride, 14, to the final diene complex involves two steps: a Fe \rightarrow



C hydrogen migration and a C-C bond cleavage. It seems unlikely that H migration would occur first since this would lead Scheme III



to a very strained, trans-fused ferrabicyclopentane. A more plausible mechanism involves initial C-C cleavage following by reductive elimination.²⁹ The conversion of 14 to 15 must involve a disrotatory ring opening with bending of the breaking σ bond toward the metal in order to explain the formation of ((*E*)-1phenylbutadiene)iron tricarbonyl (R₁ = Ph, R₂ = H) from 2phenylmethylenecyclopropane. Interestingly, the same stereochemical mode would explain the conversion of trans Feist's ester iron tetracarbonyl to the corresponding (*Z*)-diene complex¹⁶ (R₁ = R₂ = CO₂Me).

In order for the mechanism to apply to cis Feist's ester iron tetracarbonyl, it is necessary to postulate a preliminary isomerization from the known¹⁷ endo configuration to an exo configuration, since the endo isomer would be unable to undergo intramolecular hydrogen migration. This hypothesis is strongly supported by the observation¹⁶ that the ester function on C1 on the final diene complex now adopts an *E* configuration, as required by the disrotatory-toward ring opening of the η^3 -allyl complex (see Scheme III). The endo-exo isomerism of the (methylenecyclopropane)iron tetracarbonyl complex might occur by a dissociation-recombination mechanism or by direct ligand exchange with a second Fe(CO)₄ unit.

Conclusion

It seems probable that the mechanism we have proposed for the reactions of phenyl-substituted methylenecyclopropanes with iron carbonyls may, in fact, have broader application, including the Feist ester reactions.

If our mechanism is correct, then the role of frontier orbital symmetry in determining the stereochemistry of formation of the trimethylenemethane complexes would appear to have been established. This, too, may have broader implications for other types of pericyclic reaction occurring within the coordination sphere of a transition metal.

Experimental Section

¹H NMR spectra were obtained on either a Varian A60-A (60 MHz) or a Varian EM390 (90 MHz) spectrometer. ¹³C NMR spectra were recorded on a Varian CFT 20 instrument. Chemical shifts for both ¹H and ¹³C NMR are reported in parts per million (ppm) downfield from internal tetramethylsilane. Infrared spectra were obtained with either a Perkin-Elmer 700 or Perkin-Elmer 337 spectrometer. Mass spectra were recorded on a Finnigan 3300 instrument with peaks reported by *m/e* and percent relative abundance. Preparative gas chromatography was performed on a Varian Aerograph A90-P analytical gas chromatography on a Hewlett-Packard 700. Both instruments have thermal conductivity detectors and used helium as carrier gas. Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected.

Preparative layer chromatography was performed on 20×20 cm glass plates coated with a 1 mm thick layer of silica gel or alumina, with a fluorescent indicator. Column chromatography, unless otherwise indicated, was performed by using a polyethylene dry column packed with Fisher Scientific 100–200 mesh florisil, Woelm neutral alumina, or Grace Division Chemical 60–200 mesh silica gel. After development of the

⁽²⁸⁾ When (benzylideneacetone)iron tricarbonyl is used as the $Fe(CO)_3$ source, loss of the enone ligand is presumably an unassisted unimolecular process.

⁽²⁹⁾ In order to avoid the implausible formation of a free $Fe(CO)_3$ unit during the reductive elimination, one can postulate prior coordination to the free alkene in 15.

chromatogram, the column, was cut and the product eluted from the appropriate section with ether or benzene.

The term "short-path distillation" refers to a distillation using a Kontes brand short-path distillation apparatus. The distillate was collected in an air- or ice-cooled receiver.

Photolyses were performed by using an Ace Hanovia 450-W highpressure mercury lamp, filtered as indicated. Tetrahydrofuran and benzene were distilled from sodium benzophenone ketyl under nitrogen. Hexane, pentane, dimethylformamide, and benzene- d_6 were distilled from calcium hydride. Triethylamine and pyridine were distilled from barium oxide. Dimethyl sulfoxide was distilled under vacuum from sodium hydroxide onto activated 3A molecular seives.

Alkyllithium reagents were titrated with diphenylacetic acid just prior to use. All other reagents were used without purification, except where indicated.

2-Phenylmethylenecyclopropane. This was prepared by the method of Arora and Binger:²⁴ ¹H NMR (CDCl₃) δ 1.2 (m, 1), 1.7 (m, 1), 2.5 (m, 1), 5.6 (m, 2), 7.2 (m, 5); ¹³C NMR (CDCl₃) 14.6, 20.2, 104.4, 125.8, 126.3, 128.3, 135.4, 141.9 ppm; mass spectrum, *m/e* (relative intensity) 132 (0.5), 131 (10.6), 130 (100), 129 (17.0), 128 (1.5).

(Benzylideneacetone)iron Tricarbonyl. This was prepared by the method of Lewis et al. 22

Reaction of 2-Phenylmethylenecyclopropane with Fe₂(CO)₉. In a typical run Fe₂(CO)₉ (1.53 g, 4.2 mmol), 2-phenylmethylenecyclopropane (0.54 g, 4.1 mmol), and benzene (15 mL) were added to a 50-mL round-bottom flask and stirred for 20 h under argon. The solution was then filtered and the solvent removed on a rotary evaporator. The residue was purified by column chromatography on activity III alumina (for product separation and identification) or florisil (for measurement of the ratio of 2:3, since they were not separated under these conditions) with pentane/benzene. On alumina the bottom (largest R_f) band was (phenyltrimethylenemethane)iron tricarbonyl: ¹H NMR (C₆D₆) δ 1.4 (2 peaks with an area ratio of 3.4:1, 2, 1.9 (d, 1, J = 2.5 Hz), 2.6 (d, 1, J = 2.5 Hz), 2.5 (d, 1, J = 2.5J = 4.5 Hz), 3.9 (d, 1, J = 2.5 Hz), 6.9–7.1 (m, 5); ¹H NMR (CS₂) δ 1.8 (doublet with a singlet in the middle, 2, J = 4.5 Hz for the doublet), 2.3 (d, 1, J = 2.5 Hz), 2.8 (d, 1, J = 4.5 Hz), 4.2 (d, 1, J = 2.5), 7.1 (s, 5); mass spectrum, m/e (relative intensity) 272 (1.0), 271 (5.9), 270 (36.9), 268 (3.3), 243 (11.3), 242 (71.1), 214 (21.0), 187 (12.7), 186 (90.0), 161 (11.3), 160 (100).

The middle band was ((*E*)-1-phenylbutadiene)iron tricarbonyl: ¹H NMR (C_6D_6) δ 0.1 (dd, 1), 1.3 (dd, 1), 1.7 (d, 1), 4.6 (m, 1), 5.2 (dd, 1), 7.0-7.4 (m, 5).

At the top of the column was an unidentified compound (or mixture of compounds): ¹H NMR (CS₂) δ 1.4 (m, 1.5), 2.1 (m, 1.0), 3.7 (m, 1.5), 7.3 (m, 5.0); IR (CS₂ solution) 2800–3100 (w), 2050 (m), 1980 (s), 1725 (m), 1680 (m) cm⁻¹, and many bands below 1500 cm⁻¹; mass spectrum, m/e (relative intensity) 373 (2.1), 372 (8.9), 346 (10.2), 345 (27.8), 344 (100), 260 (11.5), 186 (10.5), 184 (15.6), 183 (39.5), 105 (51.2), 91 (72.4).

Reaction of 2-Phenylmethylenecyclopropane with $Fe(CO)_5/(CH_3)_3NO$. To a three-neck flask under argon was added 2-phenylmethylenecyclopropane (0.11 g, 0.85 mmol), anhydrous $(CH_3)_3NO^{30}$ (0.43 g, 5.7 mmol), and benzene (10 mL). The solution was cooled in ice/water and $Fe(CO)_5$ (0.3 mL, 2.3 mmol) added. The solution was stirred cold for 15 min and then overnight at room temperature. The solution was then filtered and the solvent removed on a rotary evaporator. The residue was purified by chromatography, as above.

Reaction of 2-Phenylmethylenecyclopropane with (Benzylideneacetone)iron Tricarbonyl. 2-Phenylmethylenecyclopropane (0.15 g, 1.15 mmol) and (benzylideneacetone)iron tricarbonyl (0.33 g, 1.15 mmol)were stirred at room temperature in benzene (10 mL) for 4 days under nitrogen. The solvent was removed on a rotary evaporator and the residue purified by preparative layer chromatography on silica gel with pentane.

Styrene-2-d. Styrene-2-d, either cis or trans, was prepared by the Berson modification³¹ of Zweifel's procedure.³² Since the next reaction could not be made to work reproducibly in the presence of phenylacetylene, an extra purification step was added. It was as follows.

The mixture of styrene-2-d and its phenylacetylene contaminant³² was placed in a three-neck flask and cooled in an ice/water bath. Ether (5 mL), sodium hexamethyldisilazide (1.2 mmol), and benzophenone (1.2 mmol) were added per millimole of phenylacetylene. The reaction was stirred at 0 °C for 30 min and then allowed to warm slowly to room temperature overnight. Methanol (50 mL) was added and the mixture

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stirred at room temperature for 2 h. The resulting solution was diluted with ether (50 mL), washed with water (3×50 mL), and then dried over anhydrous MgSO₄. The ether was removed on a rotary evaporator and the residue purified by short-path distillation; bp 51-54 °C (20 torr).

1,1-Dibromo-2-phenylcyclopropane-3-d. This was prepared from styrene-2- d_1 and phenyl(tribromomethyl)mercury by the procedure described.³³ for 1,1-dibromo-*trans*-2.3-diphenylcyclopropane. The fraction boiling at 84-86 °C (0.3 torr) was collected. Isolated yields were typically 50%: ¹H NMR (CDCl₃) δ 1.9 (m, 1), 2.9 (m, 1), 7.2 (s, 5) for trans δ and 2.1, 2.9 and 7.2 for cis.

1-Bromo-2-phenyl-1-cyclopropane-3-d-carboxylic Acid.³⁴ To a three-neck flask under nitrogen was added 1,1-dibromo-2-phenylcyclopropane-3-d (10.1 g, 36.4 mmol) and THF (175 mL). The solution was cooled in a toluene/liquid nitrogen slush bath and treated with a hexane solution of tert-butyllithium (32 mL of 1.14 M, 36.5 mmol) over 30 min. The resulting deep red solution was stirred for an additional 30 min and then subjected to a stream of carbon dioxide for 15 min. When the solution had become yellow, it was allowed to warm slowly to room temperature and was then stirred for 4 h. The reaction mixture was added to a separatory funnel containing water (100 mL) and ether (100 mL) and shaken. The organic layer was extracted with saturated aqueous sodium bicarbonate (2×50 mL), and the extracts were combined with the aqueous layer from the original separation. The aqueous solution was acidified (pH <1) with 3 M hydrochloric acid and extracted with ether $(4 \times 100 \text{ mL})$. The ether extract was dried over anhydrous MgSO₄ and the solvent removed on a rotary evaporator. The residue was recrystallized from hexane/ether in an ice/methanol bath to give 4.74 g (54%) of the product: mp 92-94 °C; ¹H NMR (CDCl₃) δ 1.8 (m, 0.1), 2.2 (d, 0.9), 3.1 (m, 1.0), 7.2 (s, 5.0), 10.3 (s, 1.0) for trans and δ 1.8 (m, 0.9), 2.2 (m, 0.1), 3.1 (m, 1.0), 7.2 (s, 5.0), 9.4 (s, 1.0) for cis.

(1-Bromo-2-phenyl-1-cyclopropyl-3-d)methanol. 1-Bromo-2-phenyl-1-cyclopropane-3-d-carboxylic acid was converted to its methyl ester by treatment with diazomethane by the method of Semmelhack et al.,³⁵ except that dichloromethane was used as solvent instead of ethanol. The product was obtained in 89% yield.

To a three-neck flask was added lithium aluminum hydride (0.16 g, 4.0 mmol) and ether (50 mL). The suspension was cooled to 0 °C and the methyl ester (1.02g, 4.0 mmol) added over 15 min. After the mixture was stirred at 0 °C for 3 h, ether (40 mL) and saturated aqueous sodium sulfate (40 mL) were added. The mixture was allowed to warm to room temperature, the organic and aqueous layers were separated, and the aqueous layer was extracted with ether (3 × 30 mL). The combined ether layers were dried over anhydrous MgSO₄, and the solvent was removed on a rotary evaporator. The residue (0.8 g, 90%) was used without further purification: ¹H NMR (CDCl₃) δ 1.6 (m, 1.0), 1.8 (b s, variable integration), 2.9 (m, 1.0), 3.5 (s, 2.0), 7.3 (s, 5.0) for trans and a similar spectrum for cis.

2-Phenylmethylenecyclopropane-3-d. (1-Bromo-2-phenyl-1-cyclopropyl-3-d)methanol was converted to its methane sulfonate ester (mesylate) by a method analogous to that of Crossland and Servis.³⁶ A 90% yield was obtained.

The mesylate (0.37 g, 1.21 mmol) and THF (30 mL) were added to a three-neck flask under nitrogen. The solution was cooled in a toluene/liquid nitrogen slush bath and a hexane solution of *tert*-butyllithium (1.1 mL of 1.14 M, 1.25 mmol) added over a period of 25 min. The dark red solution was stirred and allowed to warm to room temperature over a period of 3 h. The reaction mixture was then diluted with pentane (100 mL) and washed with water $(4 \times 50 \text{ mL})$. The organic layer was dried over anhydrous MgSO₄ and the solvent removed on a rotary evaporator. The residue was purified by preparative layer chromatography with pentane or silica gel to give 0.09 g (50% yield) of 2-phenylmethylenecyclopropane-3-d: ¹H NMR (CDCl₃) δ 1.2 (m, 0.92 ± 0.8), 1.8 (m, 0.18 \pm 0.03), 2.7 (m, 1.0), 5.6 (m, 2.18 \pm 0.11), 7.3 (m, 5.0) for trans and δ 1.2 (m, 0.16 \pm 0.03), 1.8 (m, 0.98 \pm 0.04), 2.7 (m, 1.0), 5.6 (m, 1.94 0.06), 7.3 (m, 5.0) for cis;³⁴ ¹³C NMR (CDCl₃) {¹H} 14.6 (t), 20.2 (s), 104.4 (s), 125.8 (s), 126.3 (s), 128.3 (s), 135.4 (s), 141.9 (s) (same spectrum for both isomers); mass spectrum, m/e (relative intensity) 133 (3.1), 132 (33.4), 131 (100), 130 (30.3), 129 (4.6), 128 (0.5) for trans.

(E)-1-Phenyl-3-propenol-3,3-d₂. A slurry of methyl cinnamate (15.0 g, 93 mmol), LiAlD₄ (3.9 g, 100 mmol), and hexane (250 mL) was

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(36) The integration data for the cis isomer are different from those given

⁽³⁶⁾ The integration data for the cis isomer are different from those given previously²⁷ because the experiment was repeated under more carefully controlled conditions and better deuterium incorporation was achieved.

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heated to 60 °C for 16 h under nitrogen. The reaction was quenched with methanol (25 mL) and water (10 mL). After addition of 5% HCl (125 mL), the mixture was filtered. The solid was washed with ether (150 mL) and the aqueous layer extracted with chloroform (125 mL). The combined organic layers were dried over anhydrous MgSO₄ and evaporated to give (E)-1-phenyl-3-propenol-3,3-d₂ (8.32g, 66%): ¹H NMR (CDCl₃) δ 4.15 (s, 1), 6.45 (AB q, 2), 7.3 (m, 5). (E)-3-Phenyl-1-propenone-1-d. A slurry of (E)-1-phenyl-3-

(E)-3-Phenyl-1-propenone-1-d. A slurry of (E)-1-phenyl-3propenol-3,3- d_2 (7.82 g, 57 mmol) and active MnO₂ (80 g) in CCl₄ (30 mL) was stirred under nitrogen overnight at room temperature. the mixture was filtered and the solid extracted with ether (250 mL). The combined CCl₄ and ether extracts were evaporated. The residue was distilled under aspirator vacuum to give (E)-3-phenyl-1-propenone-1-d (5.12 g, 66%): ¹H NMR (CDCl₃) δ 6.6 (d, 1), 7.3 (m, 6).

 $((\vec{E})$ -1-Phenylbutadiene-3-d)iron Tricarbonyl. Triphenylmethylphosphonium bromide (6.49 g, 18 mmol) and ether (40 mL) were stirred under nitrogen in a three-neck flask at room temperature. A hexane solution of *n*-butyllithium (18 mmol) was added over a period of 5 min and the solution stirred at room temperature for 4 h. (*E*)-3-Phenyl-1propenone-*1*-d (2.4 g, 17 mmol) was added dropwise and the solution refluxed overnight. The reaction mixture was cooled and filtered. The residue was washed thoroughly with ether, and the washings were combined with the original filtrate. After removal of the solvent on a rotary evaporator, the residue was purified by preparative layer chromatography with pentane on silica gel to give (*E*)-1-phenylbutadiene-3-d (0.57 g, 24%): ¹H NMR (CDCl₃) δ 5.1 (m, 2), 6.5 (m, 2), 7.2 (m, 5).

(*E*)-1-Phenylbutadiene-3-d (0.4 g, 31 mmol) and Fe₂(CO)₉ (2.3 g, 63 mol) were stirred under nitrogen in benzene (20 mL) for 24 h at room temperature. The resulting mixture was filtered, the benzene evaporated off, and the residue purified by preparative layer chromatography with pentane on alumina to give ((*E*)-1-phenylbutadiene-3-d)iron tricarbonyl (0.33 g, 36%): ¹H NMR (C₆D₆) δ 0.2 (m, 1), 1.4 (m, 1), 1.7 (d, J = 9 Hz, 1), 5.2 (d, J = 9 Hz, 1), 7.0 (m, 5).

(E)-1-Phenyl-3-butenol-2-d. A 1-L, three-neck flask was equipped with a condenser, gas inlet addition funnel, and stopper. The apparatus was flame dried under nitrogen. Diisobutylaluminum hydride (36.23 g, 255 mmol) and hexane (50 mL) were introduced. Phenylacetylene-2- d^{31} (22.7 g, 220 mmol) was added slowly, with water bath cooling. The reaction mixture was then warmed to 50 °C for 6 h. After the mixture was cooled, an ether solution of methyllithium (220 mmol) was added dropwise and the reaction mixture stirred at room temperature for 1 h. Acetaldehyde (10.2 g, 230 mmol) was then added dropwise with water bath cooling of the reaction vessel. The resulting solution was quenched with water (50 mL) and stirred overnight. The suspension was filtered, the solid was washed with pentane, and the filtrate and washings were combined. The organic layer was dried over anhydrous MgSO4 and concentrated on a rotary evaporator. The residue was distilled under aspirator vacuum with all material boiling above 60 °C being collected. The residue was crude (E)-1-phenyl-3-butenol-2-d (7.69 g). No attempt was made to further purify the material.

((E)-1-Phenylbutadiene-2-d)iron Tricarbonyl. The crude (E)-1phenyl-3-butenol-2-d (6.0 g, 40 mmol), POCl₃ (11.4 g, 74 mmol), and triethylamine (6.0 g, 59 mmol) were stirred at 85 °C in pyridine (35 mL) overnight. The pyridine was evaporated off at reduced pressure and the residue dissolved in pentane. The pentane solution was washed with saturated aqueous nickelous chloride (2×50 mL) and water (3×50 mL). After removal of the pentane, the residue was purified by GC (75 °C on OV-17) to give (E)-1-phenylbutadiene-2-d (0.06 g, 1.1%). No attempt was made to improve the yield on this step: ¹H NMR (CDCl₃) δ 5.0-5.4 (m, 2), 6.3-6.6 (m, 2), 7.3 (m, 5).

The diene was converted to its iron tricarbonyl complex as before: ¹H NMR (C_6D_6) δ 0.2 (m, 1), 1.4 (m, 1), 1.8 (b s, 1), 4.7 (m, 1), 7.0 (m, 5).

2,2-Diphenylmethylenecyclopropane. To 1,1-diphenylethylene (5.4 g, 30 mmol) and 1,1-dichloroethane (15 mL, 150 mmol) in ether (100 mL) at -60 °C was added *n*-BuLi (20 mL 90% in hexane) over 1 h. The mixture was allowed to warm slowly to room temperature and then quenched with water (50 mL). The organic layer was separated, washed with saturated aqueous NaCl, dried over anhydrous MgSO₄, and concentrated on a rotary evaporator. The residue was recrystallized from methanol to give 5.0 g (68% yield) of 1-chloro-1-methyl-2,2-diphenyl-

cyclopropane: mp 63-65 °C; ¹H NMR (CDCl₃) δ 1.58 (s, 3), 1.70, 1.82 (AB q, 2), 7.4 (m, 10). Dehydrochlorination of this compound by the method of Arora and Binger²⁴ gave 3.5 g (84% yield) of 2,2-diphenyl-methylenecyclopropane: ¹H NMR (CDCl₃) δ 1.80 (m, 2), 5.50 (m, 1), 5.70 (m, 1), 7.20 (m, 10).

Single-Crystal X-ray Analysis. A crystal of (2,2-diphenylmethylenecyclopropane)iron tetracarbonyl (9) was selected from a mixture of 8 and9 which had been crystallized from ether. The crystals of 9 which appeared to be a small percentage of the total sample (the exact proportionwas not determined and varies according to preparation conditions) wereuniformly clear when viewed through a polarizing microscope, whereasthe crystals of 8 that constituted the remainder were orange when viewedat some angles. We had already determined the X-ray structure of 8 andso were looking for a crystal with a different unit cell.

Preliminary X-ray photographs showed monoclinic symmetry and accurate lattice constants a = 22.484 (9) Å, b = 10.499 (4) Å, c = 16.232 (7) Å, and $\beta = 112.02$ (4)° were determined by a least-squares fitting of 15 diffractometer measured reflections. Assuming eight molecules of composition FeC₂₀H₁₄O₄ (fw = 374.18) per unit cell gave a plausible calculated density of 0.843 g/cm³ where either one or two molecules formed the asymmetric unit, depending upon the lattice type. Systematic extinctions (*hkl* absent if h + k = 2n + 1; *hOl* absent if l = 2n + 1 suggested the space group to be C2/c with one molecule per asymmetric unit. The correctness of this choice was confirmed by the successful structure solution and refinement that followed.

All unique diffraction maxima with $2\theta < 100^{\circ}$ were measured on a four-circle diffractometer using Ni-filtered Cu Kā radiation ($\lambda = 1.54178$ Å) and a variable-speed 1° ω -scan technique. the reflection intensities were measured relatively fast (2°/min minimum scan rate) since our previous experience with crystals of 8 had shown that they decomposed rapidly under the X-ray beam. Of the 1834 reflections measured in this fashion, 1480 (80.7%) were judged observed ($F_o \geq 3\sigma(F_o)$) after correction for Lorentz, polarization, and background effects.³⁷

The coordinates of the iron atom were obtained from a sharpened, origin-removed Patterson synthesis. After partial refinement, an F_o synthesis based on this phasing model revealed the positions of the other 24 nonhydrogen atoms in the molecule. Following block-diagonal and full-matrix least-squares refinement, hydrogen positions were calculated but not varied. Full-matrix least-squares refinement in which positional and anisotropic temperature factors for the nonhydrogen atoms were varied and the anomalous contribution of Fe (3.35 electrons) was included have converged to a current crystallographic residual of 0.088/0.099 (unweighted) for the observed data. A final ΔF synthesis showed no anomalously high residual electron density peaks.

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Supplementary Material Available: Fractional coordinates and temperature factors (Table I), bond distances (Table II), bond angles (Tables III), and observed and calculated structure factors for (2,2-diphenylmethylenecyclopropane)iron tetracarbonyl (12 pages). Ordering information is given on any current masthead page.

⁽³⁷⁾ All crystallographic calculations were done on a Prime 400 computer operated by the Materials Science Center and the Department of Chemistry, Cornell University. The principal programs used were REDUCE and UNIQUE (data reduction programs, M. E. Leonowicz, Cornell University, 1978), BLS (block-diagonal least-squares refinement, K. Hirotsu, Cornell University, 1978), ORFLS (modified) (full-matrix least squares, W. R. Busing, K. O. Martin, and H. S. Levy, ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, TN), ORTEP (crystallographic illustration program, C. K. Johnson, ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, TN), BOND (structural parameters and errors, K. Hirotsu, Cornell University, 1978), and FFT-76 (modified for Patterson synthesis, G. Germain, P. Main, and M. Woolfson, University of York).