CATIONIC CYCLIZATION OF AN IRON CARBENE COMPLEX Pascale Seutet and Paul Helquist*

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Summary: A cationic iron carbene complex has been found to undergo intramolecular cationic olefinic cyclization, resulting in formation of a six-membered carbocyclic ring.

Carbene complexes of the structure $[n^5-C_5H_5(CO)(L)Fe=CR^1R^2]^+$ have proven to be very useful intermediates, especially in alkene cyclopropanations, whereas other reactions of these species have received much less attention.¹ Herein, we report a new cyclization reaction of one of these complexes. The substrate 1 was prepared by the straightforward sequence of reactions shown in Scheme 1.

SCHEME 1



Under our standard conditions for sulfonium salt formation and carbene complex formation, 1b the cyclization product 2 (eq 1) was obtained as a mixture of diastereomers in an overall yield of 60% from the Grignard reaction in Scheme 1. We could not detect any products of intramolecular cyclopropanation.² The structure of 2 was indicated by detailed high-field NMR analysis and appropriate homonuclear decoupling experiments and by ozonolysis to give the ketoaldehyde 3 (eq 2) as again identified by high-field NMR analysis.



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We rationalize the formation of 2 by either of the pathways shown in Scheme 2 involving cationic olefinic cyclizations.³ The intermediacy of carbocationic adducts such as 5 or 6 is consistent with Brookhart's evidence for related intermediates in certain cyclopropanation reactions of iron carbene complexes.⁴



In closing, the formation of **2** suggests the possibility of employing iron carbene complexes as initiators for cationic cyclizations in general. In the present example, the overall reaction of carbene complex 4 is synthetically equivalent to the use of a simple cationic methylene group as the initiator. Further studies of this new reaction are being pursued in our laboratory.

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