Competitive Pathways in the Reaction of Acetylenic Alcohols with the η^5-Cyclopentadienyl(dicarbonyl)(η^2-2-methylpropene)iron(II) Cation

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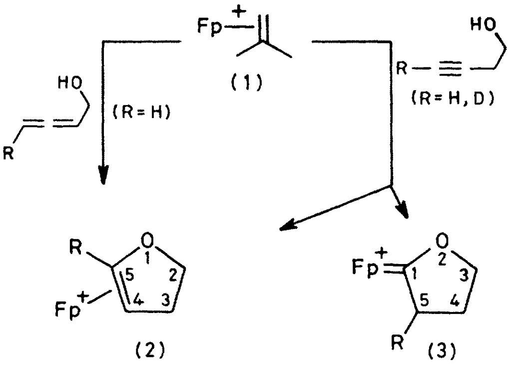
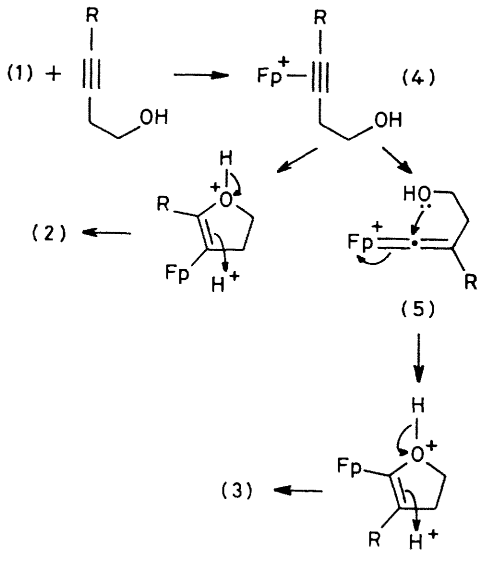
Summary The reaction of the title iron complex with but-3-yn-1-ol yields a 1 : 1 mixture of the η^2-2,3-dihydrofuran complex (**2**) and the 2-oxacyclopentylidene carbene complex (**3**) while pent-4-yn-1-ol yields the η^2-2-methylenetetrahydrofuran complex (**6**); η^2-acetylene and vinylidene carbene complexes are proposed as intermediates.



Fp = Cp(CO)$_2$Fe

THE reactions of terminal acetylenes with η^5-cyclopentadienyl(dicarbonyl)iron cation (Fp$^+$) gave several different products that were explained as arising from an intermediate η^2-acetylene complex or the rearranged vinylidene carbene complex.[1-3] We report here results which clarify the mechanisms proposed previously in these reactions and help define the relationships between the proposed η^2-acetylene and vinylidene carbene complexes through the use of an internal trapping agent.

In our previously reported reaction of buta-2,3-dien-1-ol with [Fp(η^2-2-methylpropene)]$^+$BF$_4^-$ (**1**) to give the η^2-2,3-dihydrofuran complex (**2**),[4] a mechanism involving isomerization of the allene to but-3-yn-1-ol, which then reacted with the iron complex, had to be considered. A control reaction was carried out using commercial but-3-yn-1-ol and (**1**) in 1,2-dichloroethane at 70 °C for 15 min. The clean reaction resulted in a 90% yield of a mixture of two compounds in equal amounts, which could be separated by fractional crystallization. The compounds were identified as (**2**) and the previously reported 2-oxacyclopentylidene carbene complex (**3**).[5] Since both products were stable to the reaction conditions and the allene reaction did not yield any carbene complex, the allene isomerization to the acetylene can be ruled out as a possible mechanism.

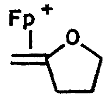


SCHEME

Plausible mechanisms for the formation of (**2**) and (**3**) from but-3-yn-1-ol are presented in the Scheme and involve initial formation of the common $[Fp(\eta^2\text{-acetylene})]^+$ intermediate (**4**) which then undergoes either internal nucleophilic attack by oxygen to give (**2**) or rearrangement to the vinylidene complex (**5**). Internal nucleophilic attack by oxygen on (**5**) produces the carbene complex (**3**) after proton transfer. Although similar steps have been proposed in related reactions,[1,2] this is the first time that simple cationic products have been isolated. Support for these mechanisms was obtained from a deuteriation study using $CD{\equiv}CH[CH_2]_2OH$ in the presence of an excess of Bu^tOH. Examination of the products by ^1H-n.m.r. spectroscopy revealed complete deuteriation at C-5 in (**2**) and loss of *ca.* 50% deuterium at C-5 of (**3**). Since no scrambling of deuterium had occurred in the production of (**2**), direct formation from the η^2-acetylene complex (**4**) was confirmed. The isomerization to the vinylidene carbene complex (**5**) is not as specific in this case as was found in the corresponding Pt example where complete hydride migration was observed.[6] Why partial loss of deuterium is observed in the present case is not clear, but it may imply different mechanisms for the Pt and Fe complexes. This possibility deserves further examination.

It is interesting that η^2-vinyl ether complexes like (**2**) were not previously isolated in reactions of cationic metal complexes with acetylenes and alcohols. Clark and Chisholm reported that but-3-yn-1-ol reacted with $[Me(PR_3)_2PtL]^+$ to give only the cationic 2-oxacyclopentylidene complex with no mention of a η^2-vinyl ether complex.[6,7] They initially proposed η^2-vinyl ether complexes as intermediates in the formation of the Pt carbene complexes,[7] but later showed that these were stable to the reaction conditions and not plausible intermediates.[6] For the Pt example, rearrangement of the intermediate η^2-acetylene complex to the vinylidene carbene complex must be faster than internal attack by oxygen on the complexed acetylene to give the predicted but unobserved η^2-vinyl ether complex.

The formation of two types of products in the reaction of the butynol with (**1**) is the first well defined example of competing nucleophilic attack on an Fe-complexed acetylene and rearrangement to a vinylidene carbene complex. This may be the only example, as pent-4-yn-1-ol yields the new η^2-2-methylenetetrahydrofuran complex (**6**) in 73% yield with no evidence of complexed acetylene rearrangement to the vinylidene carbene.



(6)

Although cationic Fp–vinylidene carbene complexes have been implicated previously in exchange reactions with terminal acetylenes,[1,2] the results presented here clearly require them as intermediates. The results also define a process for trapping the unstable cationic vinylidene carbenes as stable cyclic alkoxycarbene complexes.

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[1] S-B. Samuels, S. R. Berryhill, and M. Rosenblum, *J. Organomet. Chem.*, 1979, **166**, C9, and references cited therein.

[2] A. Davison and J. P. Solar, *J. Organomet. Chem.*, 1978, **155**, C8; and references cited therein.

[3] Stable cationic iron vinylidene complexes possessing different ligands have recently been isolated: A. Davison and J. P. Selegue, *J. Am. Chem. Soc.*, 1978, **100**, 7763; B. E. Boland, S. A. Fam, and R. P. Hughes, *J. Organomet. Chem.*, 1979, **172**, C29.

[4] D. F. Marten, Paper presented at the 33rd Southwest Regional ACS meeting, Dec. 5—7, 1977, abstract No. 174.

[5] C. H. Game, M. Green, J. R. Moss, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1974, 351.

[6] M. H. Chisholm and H. C. Clark, *J. Am. Chem. Soc.*, 1972, **94**, 1532.

[7] M. H. Chisholm and H. C. Clark, *Chem. Commun.*, 1970, 763.