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Preliminary communication

BENZOCYCLOBUTENYLIDENE-h^5-CYCLOPENTADIENYLDICARBONYLIRON(II). A HYDRIDE ABSTRACTOR MORE SPECIFIC THAN THE TRIPHENYLCARBENIUM ION

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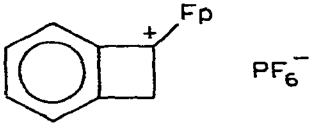
Summary

Benzocyclobutenylidene-h^5-cyclopentadienyldicarbonyliron(II) hexafluorophosphate converts h^5-CpFe(CO)$_2$R (R = cyclo-C_3H_5, CH_2-cyclo-C_3H_5) to the respective allene and butadiene complexes whereas Ph_3C^+ primarily yields addition products, both carbenium ions add to h^1 -allyl- and substituted h^1 -allyl-iron complexes with the exception of the 3,3-dimethylpropenyl complex which is converted in both cases to h^5-CpFe(CO)$_2$(CH_2=CHCMe=CH_2)$^+$.

Recently we reported the preparation and some chemical properties of h^1-benzocyclobutenylidene-h^5-cyclopentadienyldicarbonyliron hexafluorophosphate (I) [1], a metallocarbenium* ion lacking heteroatom stabilization. In particular we observed that I possessed a reactivity that paralleled that of its progenitor $Ph_3C^+PF_6^-$ Thus I reacts rapidly with nucleophilic reagents (water, methanol) to initially yield addition products. More importantly, like Ph_3C^+, I is also a hydride abstractor capable of converting cycloheptatriene to the tropylium ion and ethyl-h^5-cyclopentadienyldicarbonyliron to the corresponding cationic ethylene salt Examination of a reasonable model of I showed that the carbenium carbon was highly shielded lying near the face of the hemisphere of



(I)

Fp = h^5- CpFe(CO)$_2$

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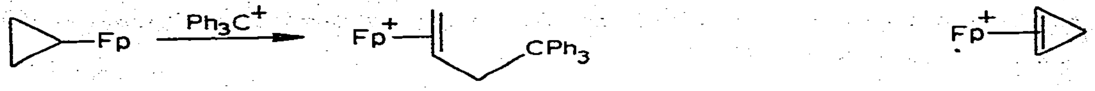
[*] Traditionally, these substances have been referred to as carbene complexes. However, the reactions described herein are those of a carbenium ion Hence we feel the name metallocarbenium ion is more appropriate.

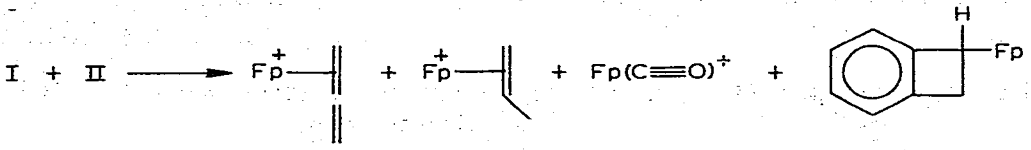
atoms that comprise the iron group. Although Ph_3C^+ presumably has a propellor shape, the carbenium carbon appears to be more exposed than that in I. Therefore it was anticipated that I might function as a more specific hydride abstractor attacking the most exposed although not necessarily the most reactive hydrogen in a ligand of an organometallic complex. We now wish to report that our expectations have come to fruition.

It appeared that the cyclopropyl ligand in II would offer a convenient entry into complexes containing the cyclopropene, h^1-cyclopropenyl, h^3-cyclopropenyl ligands [2]. Although in principle the transformation of II to the cyclopropene complex (IV) could be effected by β-hydride abstraction using Ph_3C^+, only the addition product (III) was obtained in high yield when II was treated with Ph_3C^+. It was reasoned that a hindered carbenium ion would be forced to attack hydrogen rather than carbon and possibly form the desired



(II) (III) (IV)

cyclopropene complex (IV). Consequently the reaction between I and II was examined. When I was allowed to react with II in methylene chloride for 4 days at room temperature, an orange-yellow precipitate formed which was shown by NMR and infrared spectroscopy to be the allene salt (V) admixed with varying amounts of the acidolysis product (VI) and $Fp(C{\equiv}O)^+$. Chromatography of the methylene chloride soluble fraction gave VII in better than 80% yield. Interestingly, the only hydride abstraction product is the allene complex (V)

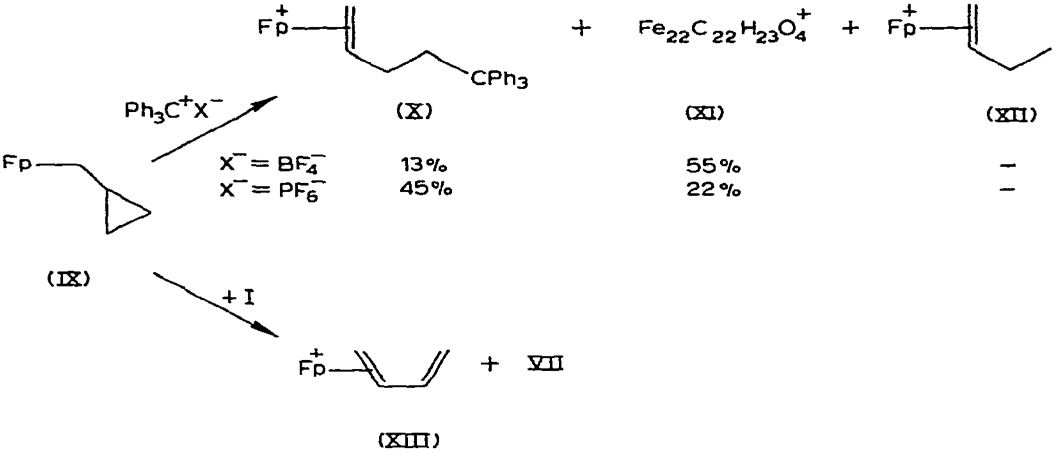


(V) (VI) (VII)

rather than the isomeric cyclopropene complex (IV).

Another example of the selectivity of I compared to Ph_3C^+ as a hydride abstractor is provided by the reactions between these carbenium ions and the cyclopropylmethyl complex (IX). Thus treatment of IX with Ph_3C^+ gave the addition product (X), an unidentified binuclear product (XI) (no incorporation of Ph_3C^+) and traces of the acidolysis product (XII). The relative amounts of X and XI are very dependent on whether the BF_4^- or PF_6^- salt is used in the reaction. Normally the two trityl salts have been used indiscriminantly; however, these results clearly indicate the potential for different reactivities based upon variations in the counter ion. In contrast to the reaction between $Ph_3C^+X^-$ and IX, I reacts with IX to afford the butadiene complex XIII in over 60% yield. The addition product XIV was not isolated or observed in the reaction mixture.

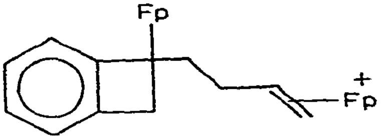
The formation of the allene complex (V) and the butadiene complex (XIII) is best interpreted in terms of respective α- and γ-hydride abstractions by I concomitant with the opening of the three-membered ring of the cyclopropyl and cyclopropylmethyl ligands of II and IX.



(X) (XI) (XII)

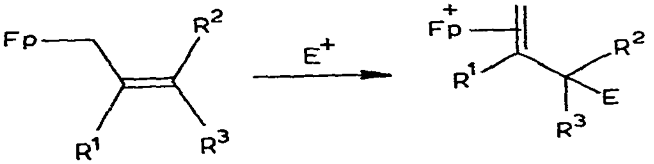
(IX)

(XIII)



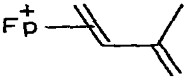
(XIV)

There appears to be no distinction between the reactivity of I and Ph_3C^+ when h^1-allyl and substituted h^1-allyl ligands are involved. Thus, both I and Ph_3C^+ add readily to VIIIa, XVa, XVIa to afford the addition products VIIIb, VIIIc, XVb, XVc and XVIb, XVIc However, the more highly substituted allyl ligand in XVII undergoes exclusive γ-hydride abstraction with either I or Ph_3C^+ to form the isoprene complex (XVIII).



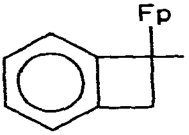
a

b, c



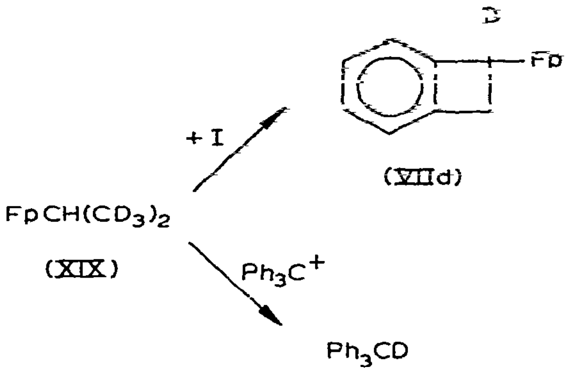
(XVIII)

VIII $R^1 = R^2 = R^3 = H$
XV $R^1 = Me, R^2 = R^3 = H$
XVI $R^1 = H, R^2$ or $R^3 = Me$
XVII $R^1 = H, R^2 = R^3 = Me$

b E = 

c E = Ph_3C—

It is evident that I has a greater propensity for hydride abstraction than Ph_3C^+. The difference in reactivities of I and Ph_3C^+ is best interpreted in terms of greater shielding of the carbenium carbon in I compared to that in Ph_3C^+. Recently published work [3] demonstrated that Ph_3C^+ is capable of initially adding hydride to one of the aromatic rings, therefore it seemed possible that I and Ph_3C^+ react at dissimilar positions. To further investigate this possibility



XIX was treated with I and Ph_3C^+. In both cases the deuterium was incorporated onto the carbenium carbon with no evidence of deuteration of either the cyclopentadienyl or benzene rings Since the reactive sites in I and Ph_3C^+ are similar, the difference in their reactivity must be attributed to steric factors.

It appears that the use of I as a hydride abstractor may be a synthetically useful alternative to the use of Ph_3C^+ especially in the instances when the latter reagent results in addition or undesired hydride abstraction

Acknowledgment

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