A General Route to $[h^5\text{-}C_5H_5Fe(CO)_2(olefin)]^+BF_4^-$ Complexes

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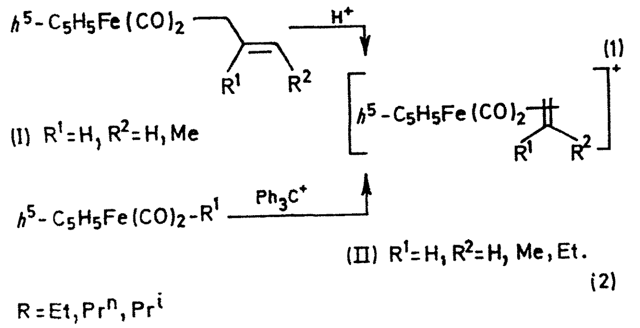
Summary Metal–olefin cations of the type $[h^5\text{-}C_5H_5Fe(CO)_2(olefin)]^+$ may readily be prepared by treatment of the complex $[h^5\text{-}C_5H_5(CO)_2(isobutene)]BF_4$ with an excess of olefin.

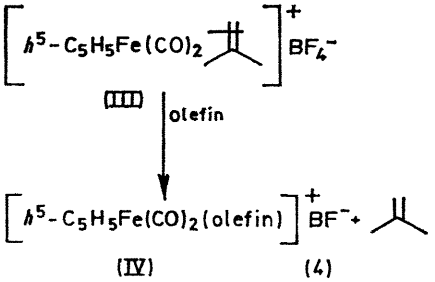
ALTHOUGH olefin exchange and displacement reactions in transition-metal–olefin complexes are well known, and the kinetics and equilibria for these processes have been determined for a variety of such complexes,[1] comparatively little use has been made of the exchange reaction as a general preparative tool.[2]



A number of olefin complexes of the general structure $[h^5\text{-}cpFe(CO)_2(olefin)]X$ have been described. These have been prepared either by protonation of the related h^1-allyl complexes[3] (eq. 1), by hydride abstraction from an alkyl complex[4] (eq. 2) or by treatment of $h^5\text{-}C_5H_5Fe(CO)_2Br$ with an olefin in the presence of a strong Lewis acid, the most efficacious being $AlCl_3$[5] (eq. 3).

$$h^5\text{-}C_5H_5Fe(CO)_2Br + \text{olefin} \longrightarrow h^5\text{-}C_5H_5Fe(CO)_2(\text{olefin})^+ \qquad (3)$$

We now report a general and very convenient method for the preparation of these complex metal–olefin cations through the exchange process:



The isobutene complex (III) is itself readily prepared in good yield from the h^1-methallyl complex (I; R^1 = Me,

$R^2 = H$) by protonation with fluoroboric acid.[6] The salt may be recrystallized from methylene chloride solution as yellow-orange platelets. These are oxidatively stable and may be stored at room temperature for prolonged periods of time without apparent decomposition.

A variety of olefin complexes (IV; olefin = ethylene, cyclohexene, cyclohexa-1,3-diene, cyclohexa-1,4-diene, cycloheptene, cyclo-octene, norbornadiene) as well as $[h^5\text{-}C_5H_5Fe(CO)_2PPh_3]BF_4$ are easily obtained by heating (III) briefly in dichloroethane solution in the presence of an excess of displacing olefin or PPh_3, and precipitating the product by the addition of ether.† Cyclo-octa-1,5-diene gave almost equal amounts of the 1 : 1 and 2 : 1 metal–olefin complexes. Preliminary experiments with phenylacetylene, cyclo-octatetraene, vinylene carbonate, and cycloheptatriene failed to give defineable products while benzene did not react under the mild conditions employed for the preparation of the olefin complexes.

The olefin complexes may alternatively be prepared, but in lower yields, by oxidation of $[h^5\text{-}C_5H_5Fe(CO)_2]_2$ with $AgBF_4$ in methylene chloride solution in the presence of an excess of olefin. This reaction is similar to that recently reported for the preparation of $h^5\text{-}C_5H_5Fe(CO)_2L$ (L = Me_2CO, Et_2S, Cl, ONO_2) from the dimer by oxidation with anhydrous feric perchlorate.[7]

The co-ordinatively unsaturated cation $[h^5\text{-cpFe(CO)}_2]^+$ (V) may be an intermediate in these latter processes, and possibly in the exchange reactions as well, but it must have only a transient existence since in the absence of olefin it decomposes to give $h^5\text{-cpFe(CO)}_3{}^+BF_4{}^-$ (VI).‡ When prepared in tetrahydrofuran solution by treatment of $h^5\text{-cpFe(CO)}_2Cl$ with $AgBF_4$, the cation may be isolated as the tetrahydrofuranate.

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† In general the solutions were heated at 65° until the evolution of isobutene had ceased; usually about 10 min.

‡ This is a highly convenient method for the preparation of (VI). The cation (V) has supposedly been isolated from aqueous solution as its Reinickate salt, but the reported analysis for this substance would accord with a hydrate as well. A recent report[8] claiming the isolation of the related co-ordinatively unsaturated cation $h^3\text{-}C_3H_5Fe(CO)_3^+$ as its nitrate salt has also been questioned.[9]

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