Journal of Organometallic Chemistry, 320 (1987) C44–C46
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

STABLE CATIONIC DIENE COMPLEXES OF IRON

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(Received October 16th, 1986)

Summary

Complexes having the formula $[C_5Me_5Fe(CO)\text{-}\eta^4\text{-diene}]^+BF_4^-$ have been prepared by reaction of $[C_5Me_5Fe(CO)_2THF]^+BF_4^-$ with a range of dienes. A Brönsted plot derived from the rates of addition of amine nucleophiles suggests an essentially "soft" nature for the complexed diene.

Stable cationic diene complexes are rare and while a range of complexes of molybdenum [1] and ruthenium [2] are known there are relatively few systems known for iron. With the aim of producing a system suitable for asymmetric synthesis it was decided to attempt the synthesis of a series of iron complexes.

The known iron systems are of two types. Complexes with the formula $[\eta^5\text{-dienylFe(CO)diene}]^+$ are known where the dienyl ligand is either cyclopentadienyl [3,4] or cycloheptadienyl [5]. Some of these complexes are unstable and all were prepared only in low overall yield. In an attempt to improve the stability and ease the preparation of this type of system we decided to investigate the potential of the pentamethylcyclopentadienyl ligand in this area.

Reaction of $C_5Me_5Fe(CO)_2I$ with $AgBF_4$ in THF gave $[C_5Me_5Fe(CO)_2THF]^+$. This cation when irradiated with UV-light reacts with a range of dienes in CH_2Cl_2 solution to give the complexes listed in Table 1. The yield based on the iodide is high, typically 80%, and the products show good stability relative to their cyclopentadienyl analogues. In all cases good analytical data were obtained and the crystal structure of the cyclohexadiene complex has been determined.

It was also observed that complexation of dienes to this system did not lead to conjugated diene isomerization of the type observed for complexation by tricarbonyliron species [6]. More remarkably, the system will not conjugate non-conjugated dienes. For example cyclohexa-1,4-diene is neither complexed η^4 nor isomerised by $[C_5Me_5Fe(CO)_2THF]^+$. If the analysis of diene isomerization suggested by Hoffmann is used, then the complexes would be classified as iron(II) d^6 systems with the positive charge located on the iron [7].

0022-328X/87/$03.50

TABLE 1

IR SPECTRA OF $[C_5Me_5Fe(CO)diene]^+ BF_4^-$ IN CH_2Cl_2 SOLUTION

diene	M(CO) (cm^{-1})	Yield (%)
1,3-Cyclohexadiene	2014	80
1,5-Cyclooctadiene	1990	76
1-Me-1,3-cyclohexadiene	2004	82
2-Me-1,3-butadiene	2023	85
1-OMe-1,3-cyclohexadiene	1984	81

TABLE 2

SECOND ORDER RATE CONSTANTS FOR REACTION OF $[C_5Me_5Fe(CO)diene]^+ BF_4^-$ WITH AMINES IN CH_2Cl_2 SOLUTION AT 25°C

Amine	pk_a	k_2 (dm^3 mol^{-1} sec^{-1})
Morpholine	8.7	1.76(±0.08)
N-Methylpiperazine	9.9	5.00(±0.04)
Pyrollidine	11.3	10.99(±0.01)
Piperidine	11.1	10.92(±0.02)

In an effort to assess the amount of positive charge centred on the diene carbons, the kinetics of the reactions of the cyclohexadiene cation with a series of amines were studied. Second-order rate constants are given in Table 2 and a Brönsted plot is shown in Fig. 1. The slope of this plot, 0.31, is much lower than that of 1.0 reported by Kane-Maguire for amine addition to $[dienylFe(CO)_3]^+$ cations, and this suggests an essentially soft nature for the complexed diene [8]. Efforts are being made to resolve these complexes in order to exploit their potential for asymmetric synthesis.

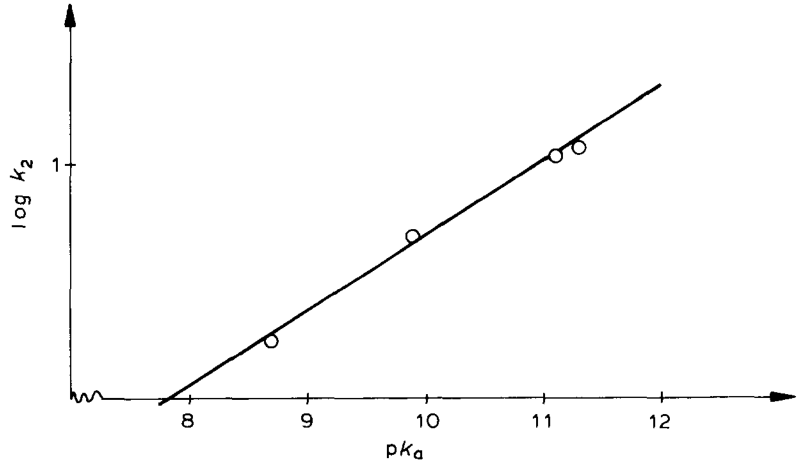

Fig. 1. Plot of log k_2 vs. pk_a of amine conjugate acid for addition of amines to $[C_5Me_5Fe(CO)\text{-}\eta^4\text{-}1,3\text{-cyclohexadiene}]^+ BF_4^-$.

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