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STUDIES ON THE REACTIVITY OF METAL π-COMPLEXES

X*. CONCERNING THE MECHANISM OF FORMATION OF THE CATIONIC TRIPLE DECKER SANDWICH COMPLEX $[Ni_2(C_5H_5)_3]^+$, AND THE ISOLATION OF $[NiC_5H_5]BF_4$

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Summary

NMR studies have been used to demonstrate the formation of the cation $[C_5H_5NiC_5H_6]^+$ in solutions of $Ni(C_5H_5)_2$ in HF. The addition of gaseous BF_3 to this cation in HF gives the ionic compound $[NiC_5H_5]BF_4$, which is a 1/1 electrolyte in nitromethane. The coordinatively unsaturated species $[NiC_5H_5]^+$ reacts with $Ni(C_5H_5)_2$ to form the cationic triple decker sandwich complex $[Ni_2(C_5H_5)_3]^+$.

Introduction

Werner and Salzer [2 - 4] have recently reported the preparation and reactions of the cation $[Ni_2(C_5H_5)_3]^+$. Preliminary results of an X-ray structural study indicate that this cation represents the first example of a triple decker sandwich complex [5]. The mechanism for the formation of this cation was postulated to involve an intermediate cyclopentadienylcyclopentadienenickel cation (I), which then reacted either by an ion—molecule reaction according to (a) or by cleavage of the diene—nickel bond and subsequent addition of an excess of nickelocene according to (b), to form the binuclear product [2,6] (see Scheme 1).

Under the conditions hitherto used for the synthesis of (III) and similar

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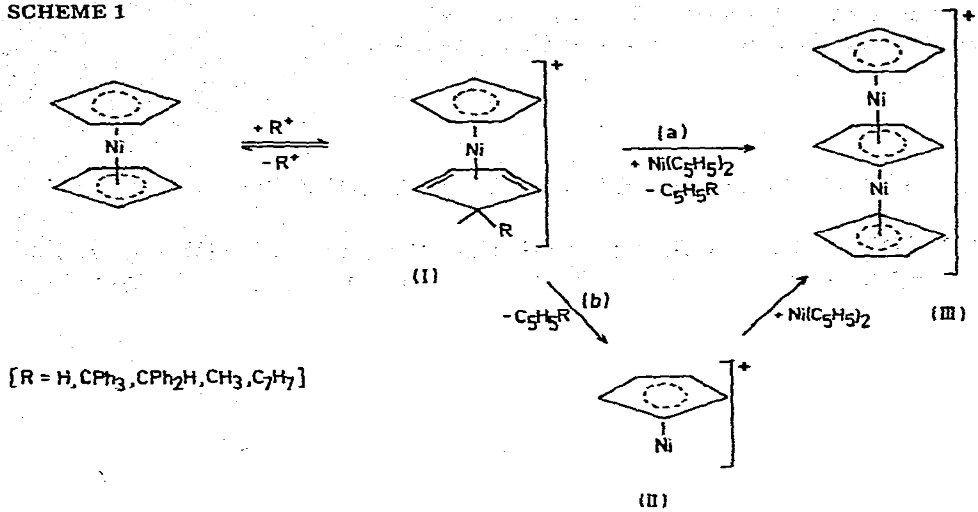
SCHEME 1



[R = H, CPh_3, CPh_2H, CH_3, C_7H_7]

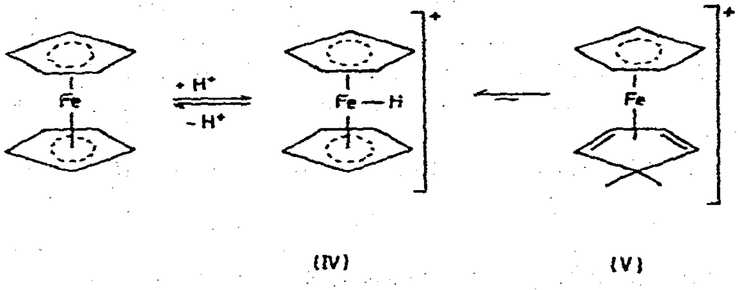
species, it is reasonable to suppose that reaction of the intermediate dienyl diene cation (I) to give (III) must be very rapid, since all previous attempts to trap this cation or to detect it by low-temperature NMR measurements have been unsuccessful.

The purpose of the present work was to verify the existence of (I) and to throw more light on the mechanism of formation of the triple decker sandwich complex.

Results and discussion

$[C_5H_5NiC_5H_6]^+$

In strong acid media, ferrocene undergoes extensive protonation at the metal atom [7]. The resulting species, $[(C_5H_5)_2FeH]^+$ (IV), which was characterised by the high field NMR resonance of the metal bonded hydrogen, must be in equilibrium with the dienyl diene cation (V) since ring proton exchange takes place in strongly acidic solution [7,8]. There is no evidence, however, that in these acid solutions the diene—iron bond can be easily split to give $[FeC_5H_5]^+$ and subsequent products. Under conditions in which $Ni(C_5H_5)_2$ reacts with HBF_4 to give $[Ni_2(C_5H_5)_3]^+$ and C_5H_6 quantitatively, $Fe(C_5H_5)_2$ is only protonated to give the cation $[(C_5H_5)_2FeH]^+$ [9].



(1)

To inhibit cleavage of the diene—nickel bond in $[C_5H_5NiC_5H_6]^+$ and any further reaction of this species with $Ni(C_5H_5)_2$ to form (III), we have studied the reactivity of nickelocene towards weaker acid systems. Following a report by Campbell [10] that HF can protonate organometallic compounds without cleaving the organic ligand—metal bonds, we used the system $Ni(C_5H_5)_2/HF$. If anhydrous HF is distilled into a tube containing a sample of freshly sublimed nickelocene a dark green solution (similar in colour to solutions of nickelocene in organic solvents) is obtained. The ^1H NMR spectrum of this solution (taken only a few minutes after mixing the reagents) clearly confirmed the formation of the cation $[C_5N_5NiC_5H_6]^+$. The solution decomposed slowly and it seems possible that even this weakly acidic medium is sufficient to promote cleavage of the diene—nickel bond and subsequent polymerisation of the liberated C_5H_6. All attempts to isolate the cation $[C_5H_5NiC_5H_6]^+$ as the fluoride or hydrogen difluoride by removal of excess HF resulted also in decomposition.

The NMR spectrum (Fig. 1) assigned to the species $[C_5H_5NiC_5H_6]^+$ consisted of resonances at δ 7.15 (relative intensity, $I = 2$), 5.80 ($I = 5$), 5.46 ($I = 2$) and 3.19 ppm ($I = 2$), the latter resonance being split into a quartet of intensity ratio 1/5/5/1. The sharp signal at 5.80 ppm is readily attributable to protons of the π-cyclopentadienyl ring whilst the remaining resonances are due to the diene ligand. The four olefinic protons of this ligand form an AA′XX′ system. The broad signal at 7.15 ppm is assigned to protons H_2 and H_3 which are also coupled to H_{exo}. The similar broad resonance at 5.46 ppm is due to H_1 and H_4 which are coupled to H_{endo} and, depending on the geometry of the cyclopentadiene ring, possibly also to H_{exo}. The coupling constants are $|J_{12} + J_{13}| \sim 2|J_{endo,1}| \sim 2|J_{exo,2}| \sim 5.0$ Hz. The lower field resonances of the

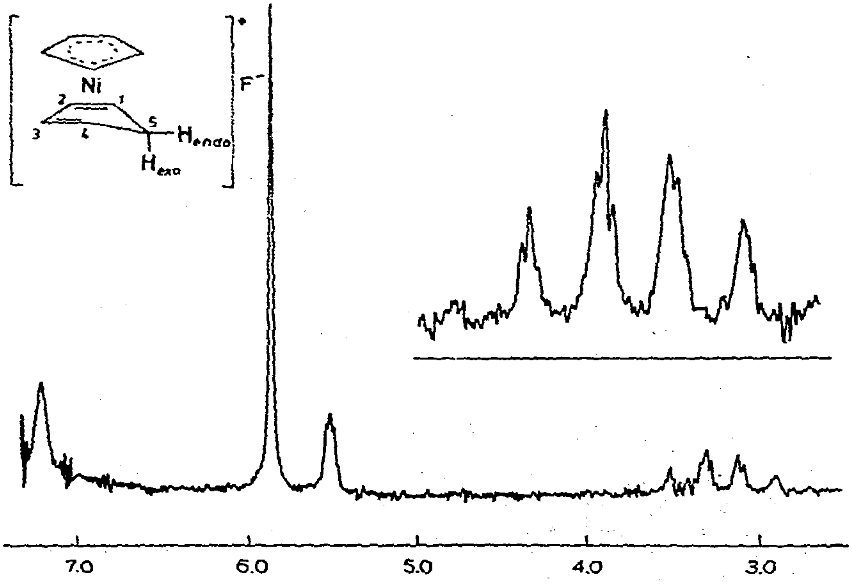


Fig. 1. NMR spectrum of $[C_5H_5NiC_5H_6]F$ in HF.

TABLE 1

CHEMICAL SHIFTS OF THE OLEFINIC AND π-CYCLOPENTADIENYL PROTONS IN THE ^1H NMR SPECTRA OF THE ISOELECTRONIC COMPLEXES $[C_5H_5Ni(Diene)]^+$ AND $C_5H_5Co(Diene)$ (in ppm)

	Diene	δ(—CH=CH—)	δ(π-C_5H_5)	Solvent	Ref.
M = Ni					
	C_5H_6	7.15[a]	5.80	HF	
	C_7H_8	5.40	5.86	CD_3NO_2	6
	C_8H_{12}	5.28	5.90	CD_3NO_2	6
M = Co					
	C_5H_6	5.25[a]	4.60	C_6H_6	12
	C_7H_8	3.37	4.45	C_6D_6	13
	C_8H_{12}	3.05	4.45	CS_2	14

[a] "Inner" olefinic protons $H_{2,3}$ (see Fig. 1).

quartet centred at 3.19 ppm and attributed to the geminal protons H_{exo} and H_{endo} with $J_{exo-endo}$ 22 Hz, are assigned to the *endo* proton the triplets being due to coupling with protons H_1 and H_4. The higher field resonances due to H_{exo} are less well resolved possibly suggesting that the ring is bent in such a way that coupling with all the protons of the AA'XX' system occurs.

It has been shown by Lewis et al. [11] that in isoelectronic complexes having the same ligands, i.e. $[C_5H_5PdC_8H_{12}]^+$ and $C_5H_5RhC_8H_{12}$, or $[C_5H_5PtC_8H_{12}]^+$ and $C_5H_5IrC_8H_{12}$, the effect of the positive charge is to shift the olefinic and π-cyclopentadienyl proton resonances downfield by about 2 and 1 ppm, respectively, relative to those resonances in the uncharged complex. We have found that this also holds for the $C_5H_5Co(Diene)$ and $[C_5H_5Ni(Diene)]^+$ series of compounds (Diene = norbornadiene, 1,5-cyclooctadiene) [6] and that the cation $[C_5H_5NiC_5H_6]^+$ fits into this scheme (Table 1).

$[NiC_5H_5]BF_4$

During our unsuccessful experiments to isolate a compound $[C_5H_5NiC_5H_6]X$, we attempted to stabilise the cation $[C_5H_5NiC_5H_6]^+$ by using a larger counterion. However, bubbling gaseous BF_3 into an HF solution of (I) immediately gave an orange coloured solution from which, after removal of excess HF, a dark brown solid, analysing as $C_5H_5NiBF_4$ (VI), could be obtained. The NMR spectrum in HF shows only one strong singlet resonance at

TABLE 2

INFRARED FREQUENCIES CHARACTERISTIC FOR THE CATION OF (VI) (IN NUJOL: OTHER BANDS OBSCURED BY NUJOL AND BF_4^- PEAKS)

Position (in cm^{-1})	Tentative assignment[a]
3120 m[b]	CH stretch
1410 m	Ring breathing
1002 s	CH deform. (‖)
872 s	CH deform. (⊥)
420 s	Ring out-of-plane deform.

[a] See ref. 16. [b] m = Medium, s = strong.

7.10 ppm which does not change its position after standing for a few hours. Addition of SbF_5 to the HF solution of $[C_5H_5NiC_5H_6]^+$ again gave a quick colour change and, after removal of HF, a brown yellow solid analysing as $C_5H_5NiSbF_6$ (VII) could be isolated.

Neither the elemental analysis nor the NMR spectra are sufficient to distinguish between formulations of (VI) and (VII) as $[NiC_5H_5]^+X^-$ or $[Ni_2(C_5H_5)_2]^{2+}[X^-]_2$. The latter species would, presumably, contain a metal—metal bond. With a view towards making this distinction we have investigated further the physical properties of (VI). The infrared spectrum of the solid (Table 2) whilst not indicating whether the cation is mono- or binuclear is similar to that of C_5H_5NiNO [15], thus supporting the assignment of the ^1H NMR signal at 7.10 ppm to a π-bonded cyclopentadienyl ring.

Attempts to obtain a Raman spectrum of (VI) produced spectra of very low quality. However, conductivity data are consistent with the presence of a 1/1 electrolyte in solution, the specific conductivities of 0.001 *M* solutions of $[Co(C_5H_5)_2]BF_4$ (used as standard) and (VI) in purified nitromethane (see ref. 17) at 25° being $1.59 \cdot 10^{-4}$ ohm^{-1}cm^{-1} and $1.56 \cdot 10^{-4}$ ohm^{-1}cm^{-1}, respectively. This proves that the cation is a mononuclear species in nitromethane solution and that the compound can be formulated as $[NiC_5H_5]BF_4$.

Other evidence for the formulation of (VI) as $[NiC_5H_5]BF_4$ comes from its reactions with triphenylphosphite and with nickelocene. In nitromethane solution, (VI) reacts instantaneously to give $[C_5H_5Ni(P(OPh)_3)_2]BF_4$ and $[Ni_2(C_5H_5)_3]BF_4$, respectively, both being characterised by elemental analysis and NMR data [2,3]. Attempts to prepare the mixed triple decker sandwich cation $[FeNi(C_5H_5)_3]^+$ (which had been observed in the mass spectra of mixed ferrocene—nickelocene [19]) by the reaction of $[NiC_5H_5]BF_4$ with $Fe(C_5H_5)_2$ in nitromethane led only to $[Fe(C_5H_5)_2]^+$. Similar experiments attempting to produce the cation $[C_8H_{12}RhC_5H_5FeC_5H_5]^+$ from $[RhC_8H_{12}]^+$ [18] and $Fe(C_5H_5)_2$ also gave $[Fe(C_5H_5)_2]^+$ [9]. The reaction of $[RhC_8H_{12}]^+$ with nickelocene in nitromethane leads to the formation of the triple decker sandwich complex $[Ni_2(C_5H_5)_3]^+$ in fairly good yields [9].

Conclusions

The present investigations strongly support the mechanistic scheme for the reactions of nickelocene with Lewis acids, particularly H^+, recently suggested by us [2,6] to explain the formation of the cationic triple decker sandwich complexes. The species $[C_5H_5NiC_5H_6]^+$ (I) postulated as a short-lived intermediate in the reaction of $Ni(C_5H_5)_2$ with HBF_4 in propionic anhydride could be clearly detected by the NMR spectrum in HF solution. Originally, in order to explain the ready formation of $[Ni_2(C_5H_5)_3]^+$ (III) we assumed that the diene—metal bond in (I) must be very labile and this assumption is supported by the instantaneous reaction of (I) with BF_3 or SbF_5 to yield $[NiC_5H_5]X$ (II). It seems likely, that (II) is in fact an intermediate in the reaction of $Ni(C_5H_5)_2$ with HBF_4 although the formation of (III) can alternatively proceed by an ion—molecule reaction of (II) and $Ni(C_5H_5)_2$ (see Scheme 1).

At present, the possibility cannot be excluded that the primary step of the reaction of nickelocene and H^+ (i.e. prior to the formation of $[C_5H_5NiC_5H_6]^+$) consists of protonation *at the metal* as it obviously occurs in the reaction of ferrocene and H^+. One may assume that for M = Ni, the equilibrium (2) is shifted to the right whereas for M = Fe it is on the left. Since the metal in

$$[(C_5H_5)_2MH]^+ \rightleftharpoons [C_5H_5MC_5H_6]^+ \qquad (2)$$

both of the preferred species, $[C_5H_5NiC_5H_6]^+$ and $[(C_5H_5)_2FeH]^+$, formally possesses an inert-gas configuration, electronic factors probably dominate the position of the equilibria. This explanation also complies with the mechanistic picture for the reactions of nickelocene with other electrophilic species which we have suggested at the beginning of that series of studies [20].

Experimental

All the experiments involving HF were carried out in KEL-F plastic apparatus and tubing. NMR measurements were made on JEOL - C - 60 - HL and Varian HA - 100 instruments and all data are relative to external $Si(CH_3)_4$. The infrared spectrum of $[NiC_5H_5]BF_4$ was recorded as a Nujol mull between AgBr windows on a Perkin - Elmer 457 spectrophotometer.

$[NiC_5H_5]BF_4$

Nickelocene (285 mg, 1.5 mmol) was dissolved in 30 ml HF and stirred for a few minutes at room temperature. Gaseous BF_3 was then bubbled into the solution which immediately changed its colour from dark green to orange. Excess HF was removed in vacuo and the remaining dark brown solid carefully dried at 20° and 10^{-3} mmHg. Yield 310 mg (98%). (Found: C, 28.56; H, 2.64; F. 34.56; Ni, 27.54. $C_5H_5BF_4Ni$ calcd.: C, 28.52; H, 2.39; F, 36.08; Ni, 27.87%.)

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