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# REACTION OF A CATIONIC CYCLOPENTADIENYLIRON ISOCYANIDE COMPLEX WITH METHYLAMINE*

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## SUMMARY

Methylamine adds to an isocyanide ligand in $(\pi\text{-}C_5H_5)(RNC)_3Fe^+$, where $R = p\text{-}CH_3OC_6H_4$, to give a complex with an amidinium ligand group:

$$(\pi\text{-}C_5H_5)(RNC)_3Fe^+ + CH_3NH_2 \rightarrow (\pi\text{-}C_5H_5)(RNC)_2Fe[C(NHCH_3)NHR]^+$$

The proton NMR spectrum indicates that the compound exists as two isomers which result from restricted rotation around the C–N bonds in the amidinium ligand.

## INTRODUCTION

In previous studies[1] we have examined reactions of coordinated carbon monoxide in cationic metal carbonyl complexes. In one investigation[2] it was found that $(\pi\text{-}C_5H_5)(CO)_3Fe^+$ reacts with primary and secondary aliphatic amines to form carbamoyl derivatives according to eqn. (1).

$$(\pi\text{-}C_5H_5)(CO)_3Fe^+ + 2RNH_2 \rightarrow (\pi\text{-}C_5H_5)(CO)_2Fe(CONHR) + RNH_3^+ \quad (1)$$

To determine whether coordinated aryl isocyanide ligands in cationic complexes were similarly reactive, the reaction of $(\pi\text{-}C_5H_5)(p\text{-}CH_3OC_6H_4NC)_3Fe^+$ with primary alkyl amines was studied. The reaction with methylamine was examined in greatest detail and yielded a product in which one molecule of amine had added to the cation, a somewhat different reaction than was observed with $(\pi\text{-}C_5H_5)(CO)_3Fe^+$.

$$(\pi\text{-}C_5H_5)(p\text{-}CH_3OC_6H_4NC)_3Fe^+ + CH_3NH_2 \rightarrow$$
$$(\pi\text{-}C_5H_5)(p\text{-}CH_3OC_6H_4NC)_2Fe[C(NHCH_3)NHC_6H_4OCH_3]^+ \quad (2)$$
(I)

The product cation, (I), was isolated as $PF_6^-$ and $BF_4^-$ salts; the compositions of these salts have been confirmed by analyses. The $PF_6^-$ salt has been shown to be a 1/1 electrolyte in nitromethane. Unlike $(\pi\text{-}C_5H_5)(CO)_2Fe(CONHR)$, compound (I) did not react with anhydrous HCl in organic solvents to remove the amine and re-

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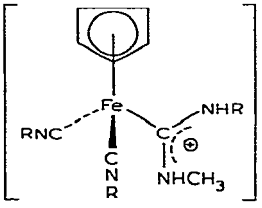
generate the cation, $(\pi\text{-}C_5H_5)(p\text{-}CH_3OC_6H_4NC)_3Fe^+$.

The assignment of structure to the product is based primarily on some recent work[3] on the reaction of amines with phenyl isocyanide ligands coordinated to $Pt^{II}$ to form a complex containing a $Pt\text{-}C(NHR)NHC_6H_5$ group.

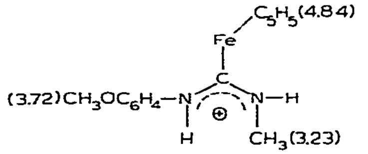
$$PtCl_2(CNC_6H_5)PEt_3+RNH_2 \rightarrow PtCl_2[C(NHR)NHC_6H_5]PEt_3$$

Similarly, the product, (I), in reaction (2) may be formulated as containing such an amidinium group.

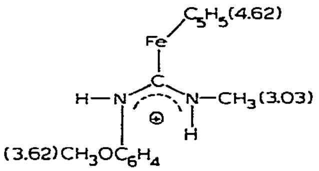


$R=p\text{-}CH_3OC_6H_4$

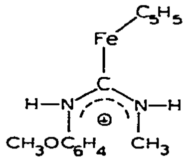
It is known in organic amidinium ions, as for example *N,N'*-dimethylacetamidinium, $CH_3C(NHCH_3)_2^+$, that there is restricted rotation around the C–N bonds as evidenced by NMR studies[4]. In the present case, restricted rotation gives four possible isomers, (Ia)–(Id):



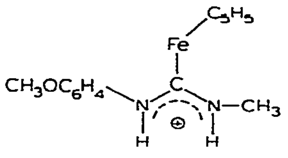
(Ia)



(Ib)



(Ic)



(Id)

Moreover, if there were restricted rotation about the Fe–C bond it is possible that each of the isomers, (Ia)–(Id), could exist as two isomers, one with the $NHCH_3$ group directed toward the $C_5H_5$ ring and the other with the $NHC_6H_4OCH_3$ group near the $C_5H_5$ ring. Of the eight possible isomers, the NMR studies suggest that only two are present (see below).

Restricted rotation around a C–N bond has been observed[5] in a related compound, $(\pi\text{-}C_5H_5)(CO)(CH_3NC)Fe[C(C_6F_5)\text{=}NCH_3]$; both isomers were isolated. Similarly both isomers of $(OC)_5Cr[C(CH_3)\text{=}NHCH_3]$ have been characterized[6].

The proton NMR spectrum of (I) as the $PF_6^-$ salt was taken in $CDCl_3$ solvent. It was much more complex than that of $(\pi\text{-}C_5H_5)(p\text{-}CH_3OC_6H_4NC)_3Fe^+$ which exhibited an aromatic multiplet at 7.17 ppm ($C_6H_4$), a singlet at 5.10 ppm ($C_5H_5$) and a singlet at 3.80 ppm ($CH_3$) with relative intensities of 12/5/9, respectively. The spectrum of (I) gave a complex multiplet in the region 6.7–7.5 ppm corresponding to the $C_6H_4$ protons with a relative intensity of 12. The five protons of the $C_5H_5$ group occur in two singlets at 4.84 and 4.62 ppm; the absorption at 4.84 is 1.6 times more intense than that at 4.62 ppm. It is assumed that these two $C_5H_5$ absorptions represent two isomers of (I).

The nine $OCH_3$ protons are split into three absorptions. By far the most intense absorption occurs at 3.76 ppm; these protons presumably correspond to the $OCH_3$ groups on the terminal isocyanide ligands. A smaller peak (3.72 ppm) on the shoulder of the 3.76 ppm absorption, and a still smaller peak at 3.62 ppm may be assigned to the $OCH_3$ protons of the $FeC(NHCH_3)NHC_6H_4OCH_3$ group in the two isomers. The three $NCH_3$ protons occur in two groups, a doublet centered at 3.23 [$J$(HNCH)∼4.5 Hz] and a broad absorption at 3.03 ppm. The former absorption is approximately 1.6 times more intense than the latter; these two bands again presumably correspond to the two isomers. These two isomers are apparently in relatively rapid equilibrium with each other since the relative intensities of the isomer absorptions were always observed to be 1.6 regardless of the reaction time used in the preparation of (I) or the number of recrystallizations used in purifying the compound. Finally, two broad absorptions at 8.06 and 7.85 ppm having a total relative intensity of one may be tentatively assigned to one of the NH protons. These two absorptions presumably correspond to the two isomers since the former absorption is approximately 1.6 times as intense as the latter.

Because of the large number of possible isomeric structures which compound (I) may have, it is difficult to make unambiguous assignments to the two isomers observed in the NMR spectrum. The organic amidinium ion, $CH_3C(NHCH_3)_2^+$, has been shown[4] to have only the structure in which one $CH_3$ group was "outside" and one was "inside" as in structures (Ia) and (Ib). It was assumed that steric factors were responsible for the absence of the structures in which both $CH_3$ groups were "outside" [as in (Id)] or both were "inside" [as in (Ic)]. The "inside–outside" structures, (Ia) and (Ib), may be assigned tentatively as the most stable forms of (I). If it is assumed that repulsion between the $CH_3$ group and the $C_5H_5$ ring is the most important structure-determining factor, isomer (Ia) would be expected to be more stable than (Ib). On this basis, structure (Ia) has been assigned to the predominating isomer in the NMR spectrum. Chemical shifts of the various protons are indicated on the structures of the major (Ia) and minor (Ib) isomers. When the $CH_3$ group is *cis* to the metal [as in (Ib)], the $CH_3$ absorption occurs at higher field than when the $CH_3$ group is *trans* to the metal [as in (Ia)]. That this was also observed for the *cis* and *trans* isomers of $(OC)_5Cr[C(CH_3){=}NHCH_3]$ gives some support to the isomeric assignments of compound (I). Nevertheless, these structural assignments must be regarded as tentative.

The presence of only two terminal isocyanide C–N stretching absorptions at 2132 (s) and 2085 (s) cm$^{-1}$ suggests that both isomers have nearly identical spectra. This was previously observed[5] to be true for the two isomers of $(\pi\text{-}C_5H_5)(CO)(CH_3NC)Fe[C(C_6F_5){=}NCH_3]$. The isocyanide C–N stretching frequencies for compound (I) compare with 2180 (s) and 2139 (s) $cm^{-1}$ for the reactant cation, $(\pi\text{-}C_5H_5)(p\text{-}CH_3OC_6H_4NC)_3Fe^+$. The decrease in C–N stretching frequencies caused by the addition of $CH_3NH_2$ to the cation is probably due to the enhanced donor properties or reduced π-bonding ability of the $-C(NHCH_3)NHC_6H_4OCH_3$ group as compared to the isocyanide ligand.

Although the product was not isolated, infrared studies indicated that ethylamine also reacts according to eqn. (2) to form the ethylamine analog of compound (I). Similar studies showed that ammonia did not react.

## EXPERIMENTAL

### *Materials*

The complex, $(\pi\text{-}C_5H_5)Fe(CO)_2Cl$, was prepared from $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ (Pressure Chemical Co.) as described in the literature[7]. Proton NMR spectra were recorded on a Varian A-60 spectrometer; chemical shifts are given in ppm downfield from the internal standard tetramethylsilane.

### *Preparation of p-methoxyphenyl isocyanide, p-$CH_3OC_6H_4NC$*

The synthesis of this isocyanide was carried out according to a reaction reported in the literature[8]:

$$p\text{-}CH_3OC_6H_4NHCHO + 2\,C_5H_5N + p\text{-}CH_3C_6H_4SO_2Cl \rightarrow$$
$$p\text{-}CH_3OC_6H_4NC + 2\,C_5H_5NH^+ + p\text{-}CH_3C_6H_4SO_3^- + Cl^-.$$

To 31.2 g of recrystallized *N*-(*p*-methoxyphenyl)formamide[9] dissolved in 160 ml of reagent-grade pyridine was added 55.4 g of *p*-toluenesulfonyl chloride. The reaction was allowed to proceed at room temperature for 25 min (longer times decrease the yield); then the reaction was stopped by adding ice. The solution was extracted four times with diethyl ether. The ether extracts were washed three times with water and dried over anhydrous $CaCl_2$ for 2 h. After filtering, the ether solution was vacuum distilled to give a 27% yield of the isocyanide product[9].

### *Preparation of $[(\pi\text{-}C_5H_5)(p\text{-}CH_3OC_6H_4NC)_3Fe]PF_6$*

Following Joshi *et al.*[10], this compound was prepared by refluxing 4.1 g of $(\pi\text{-}C_5H_5)Fe(CO)_2Cl$ and 7.4 g of $p\text{-}CH_3OC_6H_4NC$ in 150 ml of benzene for 1½ h under a nitrogen atmosphere. The benzene was then removed under water-aspirator vacuum, and the remaining residue was extracted with hot water. The hot solution was filtered and then cooled to room temperature. Upon addition of a saturated aqueous solution of $NH_4PF_6$ a voluminous yellow precipitate formed. After suction filtration, the precipitate was washed with water, diethyl ether, and finally pentane. The precipitate was dissolved in $CHCl_3$ and the solution was filtered. After adding pentane to the $CHCl_3$ solution, the mixture was cooled to −80°; this gave 11.6 g (94%) of $[(\pi\text{-}C_5H_5)(p\text{-}CH_3OC_6H_4NC)_3Fe]PF_6$ which was filtered off, washed with pentane and allowed to air-dry. The product was identified by its infrared spectrum [2180 (s) and 2139 (s) $cm^{-1}$ in a KBr pellet] in the isocyanide C–N stretching region which compares with that of 2190 (s) and 2123 (s) $cm^{-1}$ reported[10] for $[(\pi\text{-}C_5H_5)(C_6H_5NC)_3Fe]Cl$ in a KCl pellet.

The analogous salt, $[(\pi\text{-}C_5H_5)(p\text{-}CH_3OC_6H_4NC)_3Fe]BF_4$, was prepared in the same manner as the $PF_6^-$ salt except that $NH_4BF_4$ was used in place of $NH_4PF_6$ as the precipitating agent.

### *Preparation of* $\{(\pi\text{-}C_5H_5)(p\text{-}CH_3OC_6H_4NC)_2Fe[C(NHCH_3)NHC_6H_4OCH_3]\}PF_6$

Into a 150 ml diethyl ether suspension of 1.5 g of $[(\pi\text{-}C_5H_5)(p\text{-}CH_3OC_6H_4NC)_3\text{-}Fe]PF_6$ was bubbled $CH_3NH_2$. After 1 h the solid had dissolved and the flow of $CH_3NH_2$ was stopped. The solution was allowed to stir at room temperature for about 8 h during which time a yellow solid precipitated. This solid was dissolved in $CHCl_3$; the volume of the resulting solution was reduced under vacuum and a bright yellow precipitate formed upon addition of ether and pentane. The product was dried under vacuum. (Found: C, 51.0; H, 4.3; N, 7.9. $C_{30}H_{31}F_6FeN_4O_3P$ calcd.: C, 51.7; H, 4.5; N, 8.1%.) The compound gave isocyanide C–N stretching absorptions at 2132 (s) and 2085 (s) $cm^{-1}$ in a KBr pellet [at 2141 (s) and 2092 (s) $cm^{-1}$ in $CHCl_3$ solution]. The molar conductance of $\{(\pi\text{-}C_5H_5)(p\text{-}CH_3OC_6H_4NC)_2\text{-}Fe[C(NHCH_3)NHC_6H_4OCH_3]\}PF_6$ was determined at 25° on a $5.25 \times 10^{-4}$ *M* solution of the complex in nitromethane solvent. The cell constant was established using a 0.02 *M* aqueous KCl solution. A molar conductance ($\Lambda$) of 107 was obtained. This compares with values for known[11] 1/1 electrolytes at 20° of 85 and 97.

The analogous tetrafluoroborate salt, $\{(\pi\text{-}C_5H_5)(p\text{-}CH_3OC_6H_4NC)_2Fe[C\text{-}(NHCH_3)NHC_6H_4OCH_3]\}BF_4$, was prepared from $[(\pi\text{-}C_5H_5)(p\text{-}CH_3OC_6H_4NC)_3\text{-}Fe]BF_4$ in the same manner as described for the $PF_6^-$ salt. It was purified by chromatographing it on a silica gel column first using $CHCl_3$ solvent to elute a yellow impurity band and then by using acetone to elute the product. After evaporating the acetone, the product was recrystallized by dissolving it in $CHCl_3$, adding ether and pentane, and cooling to −80°. The pure product was obtained by recrystallizing it several more times in the same way. (Found: C, 56.2; H, 5.0; N, 8.5; F, 11.6. $C_{30}H_{31}BF_4\text{-}FeN_4O_3P$ calcd.: C, 56.5; H, 4.9; N, 8.8; F, 11.9%.)

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