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## Donor-Acceptor Properties of the Methyl Cyanide and Methyl Isocyanide Ligands Towards the

# Fragment CpFe(dppe)<sup>+</sup>

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### DONOR-ACCEPTOR PROPERTIES OF THE METHYL CYANIDE AND METHYL ISOCYANIDE LIGANDS TOWARDS THE FRAGMENT CpFe(dppe)<sup>+</sup>

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#### ABSTRACT

The complexes [CpFe(dppe)NCCH<sub>3</sub>]PF<sub>6</sub> and [CpFe(dppe)CNCH<sub>3</sub>]PF<sub>6</sub>, Cp =  $\eta^{5}$ -C<sub>5</sub>H<sub>5</sub>, dppe = Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>2</sub>PPh<sub>2</sub>, have been prepared and characterized. IR, <sup>1</sup>H and <sup>31</sup>P NMR and UV-Visible spectroscopic data suggest  $\sigma$ -donor behavior for the nitrile and  $\pi$  acceptor behaviour for the isonitrile ligands towards the iron fragment. Cyclic voltammetry studies of the complexes confirmed such conclusion.

#### **INTRODUCTION**

Nitrile<sup>1</sup> and isonitrile<sup>2</sup> ligands have been widely used in transition metal chemistry. Nitriles may act as  $\eta^1$  ligands coordinating through the nitrogen lone pair as well as in the  $\eta^2$  mode through the C-N  $\pi$  orbitals<sup>3</sup>. On the other hand, isonitriles



Fig. 1. Coordination Modes of Nitriles and Isonitriles in Mononuclear Systems.

may act as  $\eta^1$ -ligands through the carbon atom (except in binuclear systems where other bridging coordination modes are also possible<sup>2</sup>), as shown in Fig. 1.

Experimental<sup>1</sup> and theoretical results<sup>4</sup> have shown that nitriles are weak  $\sigma$ donor and  $\pi$ -acceptor ligands. However, the donor-acceptor properties of isonitriles vary as a function of the oxidation state of the metal and the nature of the other ligands attached to the metal<sup>2</sup>. Thus, when bound to metals in their higher oxidation state, they act as  $\sigma$  donors, while when coordinated to a low-valent metal, isonitriles act as efficient  $\pi$  acceptors.

Although numerous nitrile<sup>1</sup> and isonitrile<sup>2</sup> transition metal complexes have been reported, NCR and CNR compounds of iron are relatively rare. We have recently reported a serie of compounds [CpFe(dppe)L]PF<sub>6</sub>, Cp =  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>, dppe = Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>2</sub>PPh<sub>2</sub>, L = neutral donor ligand<sup>5</sup>.

This communication reports an example where the donor-acceptor properties of the ligands methyl cyanide and methyl isocyanide towards the fragment  $CpFe(dppe)^+$  may be compared through the preparation and characterization of the isomers  $[CpFe(dppe)(\eta^1-NCCH_3)]PF_6$ , (<u>1</u>), and  $[CpFe(dppe)(\eta^1-CNCH_3)]PF_6$ , (<u>2</u>). (See Fig. 2).

#### **RESULTS AND DISCUSSION**

The isocyanide complex was prepared by alkylation of the cyanometallate precursor<sup>6</sup> CpFe(dppe)CN according to the equation shown below:



Fig. 2. Proposed Structures for Complexes 1 and 2

#### KPF<sub>6</sub>/THF

CpFe(dppe)CN + MeI  $\longrightarrow$   $[CpFe(dppe)CNCH_3]PF_6 + KI$ R.t.

The compound is a stable yellow solid. The red N-bonded isomer,  $[CpFe(dppe)NCCH_3)]PF_6$ , was prepared by reaction of CpFe(dppe)I with  $CH_3CN$  using thallium hexafluorphosphate (TlPF<sub>6</sub>) for halide abstraction<sup>6</sup>. Although these complexes could be considered as linkage isomers<sup>7</sup>, the definition of some authors<sup>8</sup> excludes single complexes that contain ligands with different bonding modes of the atoms. N-Bonded NCCH<sub>3</sub> and C-bonded CNCH<sub>3</sub> ligands linked to the same organometallic fragment  $CpFe(dppe)^+$  may lead to the possibility to compare the donor-acceptor properties of the nitrile and isonitrile ligands.

Spectroscopic data for the complexes are displayed in Table I. These data show that  $v_{CN}$  of the nitrile ligand in the Fe complex increases with repect to that for free methyl cyanide (2252 cm<sup>-1</sup>), which indicates a release of electron density from a lone pair orbital on nitrogen. As a consequence, an induced strengthening of the C-N  $\sigma$  system ocurrs, leading to an increase in the NC stretching frequency on coordination. Similar results have been reported for other metal NCCH<sub>3</sub> complexes<sup>1,9</sup>. In contrast,  $v_{CN}$  of the isocyanide ligand in the complex decreases with respect to free methyl isocyanide (2166 cm<sup>-1</sup>) which suggests some Fe-CNCH<sub>3</sub>  $\pi$ -backbonding interaction.

From the IR data we may conclude that the nitrile ligand acts mainly as a  $\sigma$ -donor while the isocyanide ligand acts mainly as a  $\pi$ -acceptor. <sup>1</sup>H and <sup>31</sup>P NMR

#### Table I

Comparison of the Spectral and Electrochemical Data for Methyl Cyanide and its Methyl Isocyanide Isomer Complex

	[CpFe(dppe)NCCH <sub>3</sub> ]PF <sub>6</sub>	[CpFe(dppe)CNCH <sub>3</sub> ]PF <sub>6</sub>
$\nu_{_{CN}} (cm^{-1})^{a}$	2266 $(\Delta v = +14)^{d}$	2147 (Δv=-19)
$\delta^{1} H (C_{5}H_{5})^{b}$	4.48	4.53
$\delta^{31} P (dppe)^{b}$	98.7	99.5
CV (volt) <sup>c</sup>	0.84	1.15
. ,		

a) in CH<sub>2</sub>Cl<sub>2</sub> solution, b) in CDCl<sub>3</sub> solutions, in ppm, c) in CH<sub>2</sub>Cl<sub>2</sub> solution, using a calomel electrode as reference, d)  $\Delta v = v$  (complex) - v (free).

data are also in agreement with this conclusion. In fact, the higher-field signal of the ring protons of the  $C_{s}H_{s}$  group in complex (<u>1</u>), when compared with that of complex (<u>2</u>), indicates a greater Fe-L shift density in (<u>2</u>) than (<u>1</u>). The higher-field signal of the phosphorus dppe signal in (<u>1</u>) than that in (<u>2</u>) is also consistent with a greater electron density shift Fe-L in (<u>2</u>) than (<u>1</u>). In fact, cyclic voltammetry results indicate that the cyanide complex is more electron-rich than the isocyanide complex.

Cyclic voltammetry (CV) shows that each of the complexes undergoes reversible, diffusion controlled oxidation at a platinium electrode in  $CH_2Cl_2$  (Table I). The oxidation potential of the nitrile compound is less positive than that of the isonitrile ligand which indicates that the electron richness follows the order Fe-NCCH<sub>3</sub> > Fe-CNCH<sub>3</sub>.

Additional support for the donor acceptor properties of CH<sub>3</sub>CN and CH<sub>3</sub>NC towards the fragment CpFe(dppe)<sup>+</sup> arises from the UV-Visible spectra. Fig. 3 shows the room temperature electronic absorption spectra of the complexes. The spectrum for the nitrile complex exhibits a band around 450 nm ( $\epsilon = 720$ ) which is not



Fig. 3. UV-Visible Absorption Spectra of  $[CpFe(dppe)NCCH_3]PF_6$ (----) and  $[CpFe(dppe)CNCH_3]PF_6$  (--) at Room Temperature in  $CH_2Cl_2$ 

sensitive to the solvent as can be viewed from data in Table II. Thus, this absorption band is responsible for the red colour exhibited by the complex.

On the other hand, the C-bonded isocyanide complex shows a well defined absorption band at 380 nm ( $\epsilon = 910$ ) which explains the yellow color exhibited by this compound. This absorption band is also not sensitive to the solvent (see Table II).

The non-solvent effect<sup>10</sup> and the low extinction coefficient values for the Nand C-bonded complexes suggest the d-d character of these transitions.

Assignments of the observed bands can be made with the aid of previous molecular orbital calculations on  $CpFe(dppe)Cl^{10}$  and  $CpML_2X^4$  systems. For both

#### Table II

UV-Visible Data for the Methyl Cyanide-Iron and Methyl Isocyanide-Iron Complexes in Several Solvents

Solvent	ۻ	$\lambda$ max	$\lambda_{max}$	
		Nitrile Complex	Isonitrile Complex	
CHCl <sub>3</sub>	4.8	458	387	
CH <sub>2</sub> Cl <sub>2</sub>	8.9	450	384	
Acetone	20.7	457	387	
Acetonitrile	37.5	450	383	
Propanediol 1,2- carbonate	69.0	456	383	

a) Dielectric constant values from reference 11

complexes the lowest absorption band can be assigned to a metal-centered  $dz^2 \rightarrow dx^2 - y^2$  transition.

The shift of the lowest absorption band to high energy in going from methyl cyanide ligand to methyl isocyanide ligand can be explained by the greater  $\pi$  acceptor ability of isocyanide ligand than the cyanide ligand. In fact an increase of the  $\pi$  contribution of the L ligand stabilize the  $\pi$  levels (dz<sup>2</sup>,dxz, dyz) in the fragment CpFe(dppe)<sup>+</sup> which causes an increase of the HOMO-LUMO gap. Thus, considering that  $\lambda_{max}$  for the lowest d-d transition in the complexes [CpFe(dppe)L]PF<sub>6</sub> is a measure of the  $\pi$ -acceptor ability of the L ligand<sup>5,10</sup>, the following  $\pi$ -order for other ligands can be established: CH<sub>3</sub>NC  $\leq$ P(Bu-n)<sub>3</sub>  $\leq$  CH<sub>3</sub>CN  $\leq$  NR<sub>3</sub>.

#### **EXPERIMENTAL**

Infrared spectra were recorded on a FT-Bruker 66V spectrometer in Nujol. NMR spectra were recorded on a Bruker AMX 300 spectrometer in CDCl<sub>3</sub> or acetone-d<sub>6</sub> with TMS(H)  $\delta = 0.0$  ppm as internal standard or 85% H<sub>3</sub>PO<sub>4</sub>. Downfield shifts are positive with respect to the reference as external standard for the <sup>31</sup>P measurements.

UV-Visible absorption spectra were recorded using a Varian DMS-90 spectrophotometer with 1 cm optical path cuvettes.

Electrochemical measurement were made on a Parc model 370 electrochemistry system, using a three-electrode device, employing a carbon glassy working electrode, a platinum wire counter electrode and satured calomel reference electrode.

Solutions of the complexes were  $10^{-3}$  M and 0.1 M in  $(NBu_4)PF_6$  as supporting electrolyte. Under the same experimental conditions  $E_{1/2}$  for the ferrocene-ferrocenium couple was 0.45 V with a peak separation of about 0.060 V.

Reactions were carried out under nitrogen using standard Schlenk tube techniques. Diethyl ether and tetrahydrofuran were dried over sodium and distilled. Dichloromethane was dried over lithium aluminum hydride and distilled.

[CpFe(dppe)NCCH<sub>3</sub>]PF<sub>6</sub>. This compound was prepared as previously reported<sup>6</sup> from CpFe(dppe)I and NCCH<sub>3</sub> in the presence of TlPF<sub>6</sub>.

<u>[CpFe(dppe)CNCH<sub>3</sub>]PF<sub>6</sub></u>. To CpFe(dppe)CN (0.2 g, 0.28 mmol) in THF (10 mL) at room temperature was added KPF<sub>6</sub> (0.55 g, 2.9 mmol) and 0.5 mL (1.14 g, 8.0 mmol) of CH<sub>3</sub>I. The solution was stirred for 14 h at room temperature and then filtered through Kieselguhr. The solvent was removed under vacuum. The residue was extracted with CH<sub>2</sub>Cl<sub>2</sub>, filtered through Kieselguhr and the extract was concentrated under vacuum. Diethyl ether was added to precipitate the product as a yellow powder which was washed twice with diethyl ether, yield: 0.15 g, 60.0 %, melting point: 135°C (with decomposition).

Anal. found (calc.) for  $C_{33}H_{32}N_1P_3F_6Fe$  (M.W. = 704.85): 55.5 (56.2) %C; 4.47 (4.54) %H; 1.72 (1.89) %N.

<sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  ppm: 8.0-7.2 (m, C<sub>6</sub>H<sub>5</sub>), 4.53 (s, C<sub>5</sub>H<sub>5</sub>), 2.84 (s, CH<sub>3</sub>), 2.6, 2.5 (s, CH<sub>2</sub>CH<sub>2</sub>). <sup>31</sup>P NMR (CDCl<sub>3</sub>)  $\delta$  ppm: 99.5. <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  ppm: 131.5, 130.4, 129.9, 128.3 (C<sub>6</sub>H<sub>5</sub>), 80.66 (C<sub>5</sub>H<sub>5</sub>), 31.5 (CH<sub>3</sub>), 28.9 (P-CH<sub>2</sub>). IR (Nujol) cm<sup>-1</sup>: 2147(v<sub>CN</sub>), 1097 [ $\delta$ (C-H) of C<sub>5</sub>H<sub>5</sub>], 840 v(PF<sub>6</sub>), 696 [ $\delta$ (C-H) of C<sub>6</sub>H<sub>5</sub>].

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