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Coordination chemistry of $(c\text{-}C_5H_5)Fe^+$ in the gas phase at 294 ± 3 K: reactions with the inorganic ligands H_2, H_2O, NH_3, CO, N_2, NO, CO_2, N_2O, and NO_2

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Abstract

Experimental results are reported for primary and higher-order gas-phase reactions of $(c\text{-}C_5H_5)Fe^+$ with H_2, H_2O, NH_3, CO, N_2, NO, CO_2, N_2O, and NO_2. Reaction rate coefficients and product distributions were measured with the selected-ion flow tube technique operating at 294 ± 3 K and a helium buffer-gas pressure of 0.35 ± 0.01 Torr. The measurements provide intrinsic efficiencies for ligation and lead to intrinsic coordination numbers based on ligation kinetics. The extent of sequential ligation was found to be strongly dependent on the nature of the ligand. Single ligation of the $(c\text{-}C_5H_5)Fe^+$ cation was observed with H_2, N_2, N_2O, and CO_2 whereas multiple ligation was observed with NO, NO_2, CO, H_2O, and NH_3. With NO_2 oxygen-atom transfer was the dominant reaction channel. Structures have been proposed for the ligated ions and relative bond energies were investigated using multicollision induced dissociation. (Int J Mass Spectrom 204 (2001) 209–221) © 2001 Elsevier Science B.V.

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1. Introduction

Major advances have been made over the last 30 years in the determination of intrinsic reactivities for ions important in solution chemistry through experimental studies of ion–molecule reactions in the gas phase. This has been achieved for the ligation chemistry of organometallic ions, e.g. in experiments that elucidate the intrinsic kinetics and energetics of ligation and the magnitude of intrinsic coordination numbers [1–4]. The cyclopentadienyl ions $(c\text{-}C_5H_5)Fe^+$ and $(c\text{-}C_5H_5)_2Fe^+$ have received particular attention [5–11]. For example, Fourier transform mass spectrometry (FTMS) measurements have shown that $(c\text{-}C_5H_5)Fe^+$, derived from the collisional dissociation of $(c\text{-}C_5H_6)Fe^+$, is rapidly ligated with furan, thiophene, and pyrrole in Ar bath gas at static pressure of 1×10^{-5} Torr. Also, extensive ion trap measurements have been reported for the kinetics of ligation of $(c\text{-}C_5H_5)Fe^+$ derived from the ionization of ferrocene with oxygen donor ligands [H_2O, CH_3OH, $(CH_3)_2O$, iso-propanol and $(CH_3)_2CO$] as well as nitrogen-donor ligands [NH_3, CH_3NH_2, $(CH_3)_2NH$ and $(CH_3)_3N$] occurring in He bath gas at 2×10^{-4} Torr. These show a large range in efficiency and a semilogarithmic correlation was reported for the dependence of the measured rate coefficient for ligation

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on the ionization energy of the ligand for ligands with the same donor atom. Previous reports of the reactivity of Fe^+ with some of these molecules indicate either no reaction (H_2O), slow addition (NH_3, CH_3OH) or bimolecular reaction with bond redisposition [$(CH_3)_2O$, iso-propanol, CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$]. Ligated species such as the cyclopentadienylallyliron cation [$(c\text{-}C_5H_5)Fe(C_3H_4)^+$] [12] and the hydridocyclopentadienyliron cation [$(c\text{-}C_5H_5)Fe(H)^+$] [13] also have been synthesized and extensively investigated in the gas phase.

In this study we report the completion of measurements of the kinetics and energetics of the ligation of $(c\text{-}C_5H_5)Fe^+$ in He bath gas at 0.35 Torr with a variety of inorganic ligands containing hydrogen, carbon, nitrogen, and oxygen. Previous measurements in our laboratory have shown that the presence of a cyclopentadienyl ligand has a dramatic effect on the reactivity of Fe^+. For example, we have shown that the rate of ligation with N_2 [14], N_2O [15], CO [15], and NH_3 [16] is enhanced by a factor of $>10^3$, ~ 10, $>10^4$, and $\sim 10^2$, respectively, in helium bath gas at 0.35 Torr. We have also investigated the chemistry of $(c\text{-}C_5H_5)_2Fe^+$ but this ion was found to be unreactive with the ligands used in this study. The selected-ion flow tube (SIFT) technique was again used to take rate measurements since it is highly suitable for the investigation of the ligation of cations with weakly bonded ligands due to the relatively high helium pressure of the bath gas (0.35 Torr). The high number of collisions with helium atoms that result from the presence of bath gas serve both to thermalize the reacting $(c\text{-}C_5H_5)Fe^+$ ions and to stabilize the ligated collision complex formed in the reaction. This means that sequential ligation can be observed often until full coordination and at times even beyond with the formation of outershell bonds with the ligand such as hydrogen bonds as we have demonstrated in an analogous study with $(c\text{-}C_5H_5)Mg^+$ cations [17]. Moreover, with the employment of a recent modification to the SIFT technique that allows the application of multicollision induced dissociation [18], we have been able to explore the collisional de-ligation process in order to assess bond connectivities and relative ligation energies of the ligated species.

2. Experimental

The results reported here were obtained using a SIFT apparatus which has been described previously [19,20]. All measurements were performed at 294 ± 3 K and at a helium buffer-gas pressure of 0.35 ± 0.01 Torr. The reactant $(c\text{-}C_5H_5)Fe^+$ ions were generated by electron impact at 20–60 eV in a low-pressure (open) ionization source directly from pure $(c\text{-}C_5H_5)_2Fe$ vapor, or in a high-pressure (closed) ionization source from a $(c\text{-}C_5H_5)_2Fe$ vapor/Ar mixture. The ions were then mass selected, injected into the flow tube and allowed to thermalize by collisions ($\sim 4 \times 10^5$) with He buffer gas atoms before entering the reaction region downstream. About 8% of the injected $(c\text{-}C_5H_5)Fe^+$ ions were found to collisionally dissociate to produce Fe^+. The reactant neutrals were added as pure gases or, in the case of water, as a dilute (0.2%–5%) mixture in helium. The gases were obtained commercially and had a high purity (generally >99%). The water was distilled and deionized before use.

The data was analyzed in the usual fashion. Rate coefficients for primary reactions were obtained from a fit to the semilogarithmic decay of the primary ion and are estimated to have an absolute accuracy of ±30%. Higher-order rate coefficients were obtained by fitting the experimental data to the solutions of the appropriate differential equations for sequential reactions.

The SIFT operation has recently been modified in our laboratory to allow the controlled multicollision-induced dissociation (multi-CID) of ions just prior to sampling by changing the potential of the sampling nose cone. The operation, advantages and limitations of this multi-CID technique have been described in detail elsewhere [18].

3. Results and discussion

Table 1 summarizes, in order of increasing molecular weight of the ligand, the products and rate coefficients measured for the primary and higher-order ligation reactions initiated by $(c\text{-}C_5H_5)Fe^+$. All

Table 1
Measured products and rate coefficients for reactions of ground-state $(c\text{-}C_5H_5)Fe^+$ cations with selected inorganic molecules at 294 ± 3 K in helium buffer gas at a total pressure of 0.35 ± 0.01 Torr; reaction[a] and collision[b] rate coefficients are given in units of cm^3 $molecules^{-1}$ s^{-1}.

Reactant molecule	Reactant/product ions[c]	k_{exp}	k_c	k_{exp}/k_c
H_2	$(c\text{-}C_5H_5)Fe^+/(c\text{-}C_5H_5)Fe(H_2)^+$	3.6×10^{-13}	1.5×10^{-10}	0.0024
	$(c\text{-}C_5H_5)Fe(H_2)^+$/not obs.	$<1 \times 10^{-13}$		
H_2O	$(c\text{-}C_5H_5)Fe^+/(c\text{-}C_5H_5)Fe(H_2O)^+$	2.4×10^{-10}	2.3×10^{-10}	1.0
	$(c\text{-}C_5H_5)Fe(H_2O)^+/(c\text{-}C_5H_5)Fe(H_2O)_2^+$	7.5×10^{-11}		
	$(c\text{-}C_5H_5)Fe(H_2O)_2^+/(c\text{-}C_5H_5)Fe(H_2O)_3^+$	$(2 \pm\ ) \times 10^{-12}$		
	$(c\text{-}C_5H_5)Fe(H_2O)_3^+/(c\text{-}C_5H_5)Fe(H_2O)_4^+$	not observed		
NH_3	$(c\text{-}C_5H_5)Fe^+/(c\text{-}C_5H_5)Fe(NH_3)^+$	1.6×10^{-9}	2.0×10^{-9}	0.80
	$(c\text{-}C_5H_5)Fe(NH_3)^+/(c\text{-}C_5H_5)Fe(NH_3)_2^+$	3.5×10^{-10}		
	$(c\text{-}C_5H_5)Fe(NH_3)_2^+/(c\text{-}C_5H_5)Fe(NH_3)_3^+$	$(1.1 \pm 0.4) \times 10^{-12}$		
	$(c\text{-}C_5H_5)Fe(NH_3)_3^+$/not obs.	$<5 \times 10^{-14}$		
CO	$(c\text{-}C_5H_5)Fe^+/(c\text{-}C_5H_5)Fe(CO)^+$	1.1×10^{-10}[d]	7.2×10^{-10}	0.15
	$(c\text{-}C_5H_5)Fe(CO)^+/(c\text{-}C_5H_5)Fe(CO)_2^+$	1.1×10^{-10}		
	$(c\text{-}C_5H_5)Fe(CO)_2^+/(c\text{-}C_5H_5)Fe(CO)_3^+$	3.0×10^{-11}		
	$(c\text{-}C_5H_5)Fe(CO)_3^+$/not obs.	$<1 \times 10^{-13}$		
N_2	$(c\text{-}C_5H_5)Fe^+/(c\text{-}C_5H_5)Fe(N_2)^+$	2.2×10^{-11}[e]	6.5×10^{-10}	0.034
	$(c\text{-}C_5H_5)Fe(N_2)^+$/not obs.	$<1 \times 10^{-14}$		
NO	$(c\text{-}C_5H_5)Fe^+/(c\text{-}C_5H_5)Fe(NO)^+$	1.8×10^{-10}	6.6×10^{-10}	0.27
	$(c\text{-}C_5H_5)Fe(NO)^+/(c\text{-}C_5H_5)Fe(NO)_2^+$	7.7×10^{-11}		
	$(c\text{-}C_5H_5)Fe(NO)_2^+$/not obs.	$< \times 10^{-12}$		
CO_2	$(c\text{-}C_5H_5)Fe^+/(c\text{-}C_5H_5)Fe(CO_2)^+$	2.3×10^{-10}	6.8×10^{-10}	0.34
	$(c\text{-}C_5H_5)Fe(CO_2)^+$/not obs.	$<5 \times 10^{-14}$		
N_2O	$(c\text{-}C_5H_5)Fe^+/(c\text{-}C_5H_5)Fe(N_2O)^+$	2.5×10^{-10}[d]	7.4×10^{-10}	0.34
	$(c\text{-}C_5H_5)Fe(N_2O)^+$/not obs.	$<5 \times 10^{-13}$		
NO_2	$(c\text{-}C_5H_5)Fe^+/(c\text{-}C_5H_5)FeO^+ + NO$ (0.85) $/(c\text{-}C_5H_5)Fe(NO_2)^+$ (0.15)	4.5×10^{-10}	7.8×10^{-10}	0.58
	$(c\text{-}C_5H_5)FeO^+/(c\text{-}C_5H_5)FeO(NO_2)^+$	2.0×10^{-10}		
	$(c\text{-}C_5H_5)Fe(NO_2)^+/(c\text{-}C_5H_5)Fe(NO_2)_2^+$	$(1.0 \pm 0.04) \times 10^{-11}$		
	$(c\text{-}C_5H_5)FeO(NO_2)^+/(c\text{-}C_5H_5)FeO(NO_2)_2^+$	3.0×10^{-11}		
	$(c\text{-}C_5H_5)Fe(NO_2)_2^+$/not obs.			
	$(c\text{-}C_5H_5)FeO(NO_2)_2^+$/not obs.			

[a] Uncertainty in the reaction rate coefficient is less than 30%, unless indicated otherwise.
[b] Collision rate coefficient is calculated using combined variational transition-state theory [21].
[c] Branching ratios are indicated in parentheses.
[d] Previously reported [15].
[e] Previously reported [14].

rate coefficients are apparent bimolecular rate coefficients measured at 294 ± 3 K and a helium buffer-gas pressure of 0.35 ± 0.01 Torr and are compared with collision rate coefficients computed using combined variational transition-state theory [21]. The ligation is presumed to occur by termolecular association with the He buffer gas atoms acting as the stabilizing third body. However, radiative association, or a contribution by radiative association, could not be ruled out since the rate coefficients were not measured as a function of the total pressure of helium.

3.1. Reactions with H_2, N_2, CO_2, and N_2O

Only one addition was observed in the ligation of $(c\text{-}C_5H_5)Fe^+$ by these four molecules according to

$$(c\text{-}C_5H_5)Fe^+ + L + He \rightarrow (c\text{-}C_5H_5)Fe(L)^+ + He \qquad (1)$$

Experimental results for the reactions of $(c\text{-}C_5H_5)Fe^+$ with L = H_2, N_2, CO_2, and N_2O are presented in Fig. 1. There was no evidence for further ligation and, in

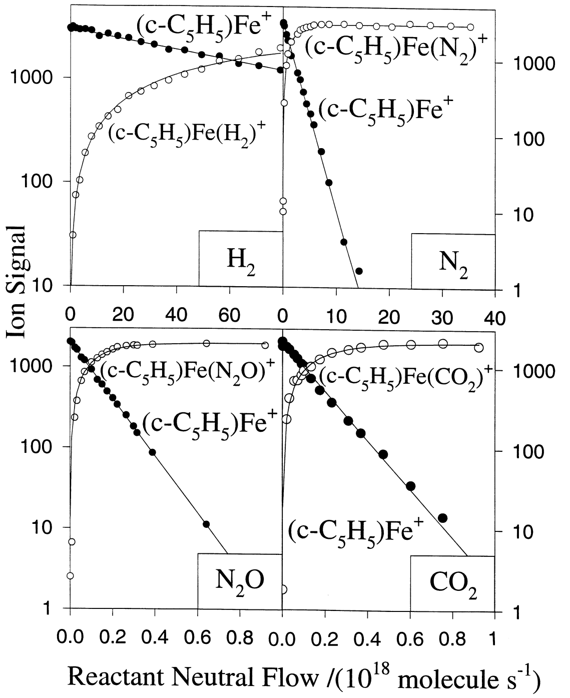


Fig. 1. Experimental data for the reactions of (c-C_5H_5)Fe^+ with H_2, N_2, N_2O, and CO_2. The measurements were performed at 294 ± 3 K and at a helium buffer-gas pressure of 0.35 ± 0.01 Torr. The lines represent fits of the experimental data for pseudo-first-order kinetics.

the reactions with CO_2 and N_2O, there was no evidence for the oxidation of iron to form (c-C_5H_5)FeO^+. The measured values for the effective bimolecular rate coefficients for these reactions were in the range from 3.6×10^{-13} to 2.5×10^{-10} cm^3 $molecule^{-1}$ s^{-1}. The rate coefficient for ligation with H_2 is the smallest. There was no indication of the attainment of equilibrium in this ligation reaction from an analysis of the variation of the product to reactant ion signal ratio as a function of H_2 addition. As a consequence, the rate coefficient for this slow ligation reaction is not reported as a lower limit. The measured upper limits to the rate coefficients of the further reactions of (c-C_5H_5)Fe(L)$^+$,

$$(c\text{-}C_5H_5)Fe(L)^+ + L + He \rightarrow \text{no reaction} \qquad (2)$$

were $k_2 < 10^{-13}$ for L = H_2 and CO_2, $k_2 < 10^{-14}$ for L = N_2 and $k_2 < 5 \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} for L = N_2O.

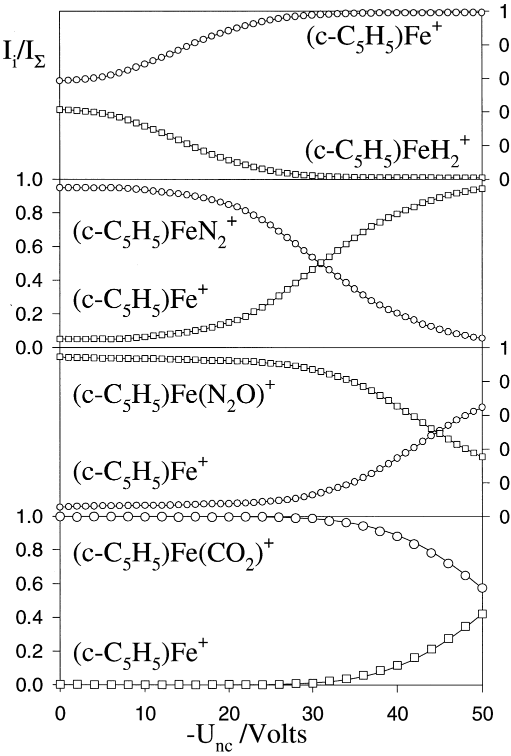


Fig. 2. Results of multi-CID experiments in the laboratory energy scale (U_{nc} is the voltage on the nose cone) for (c-C_5H_5)FeL^+ with L = H_2, N_2, N_2O, and CO_2. The reactant flow was selected in order to maximize the adduct signal. The measurements were performed with a helium buffer/collision gas at a total pressure of 0.35 ± 0.01 Torr.

The observed CID profiles of the singly ligated (c-C_5H_5)Fe(L)$^+$ product ions are shown in Fig. 2. All four dissociations lead to the elimination of the ligand according to

$$(c\text{-}C_5H_5)FeL^+ + He \rightarrow (c\text{-}C_5H_5)Fe^+ + L + He \qquad (3)$$

and the order of ligation energy is $D[(c\text{-}C_5H_5)Fe^+\text{–}H_2] < D[(c\text{-}C_5H_5)Fe^+\text{–}N_2] < D[(c\text{-}C_5H_5)Fe^+\text{–}N_2O] < D[(c\text{-}C_5H_5)Fe^+\text{–}CO_2]$. This relative order can be anchored to a lower limit for the standard free energy of deligation, $\Delta G^\circ_{294} = 7.0$ kcal mol^{-1}, which may be derived from the ion–signal ratio plot for the ligation with H_2. Production of FeL^+ was not observed over the available range in collision energy. The (c-C_5H_5)Fe^+–L bond is therefore the weakest bond in each of the four cases reported here.

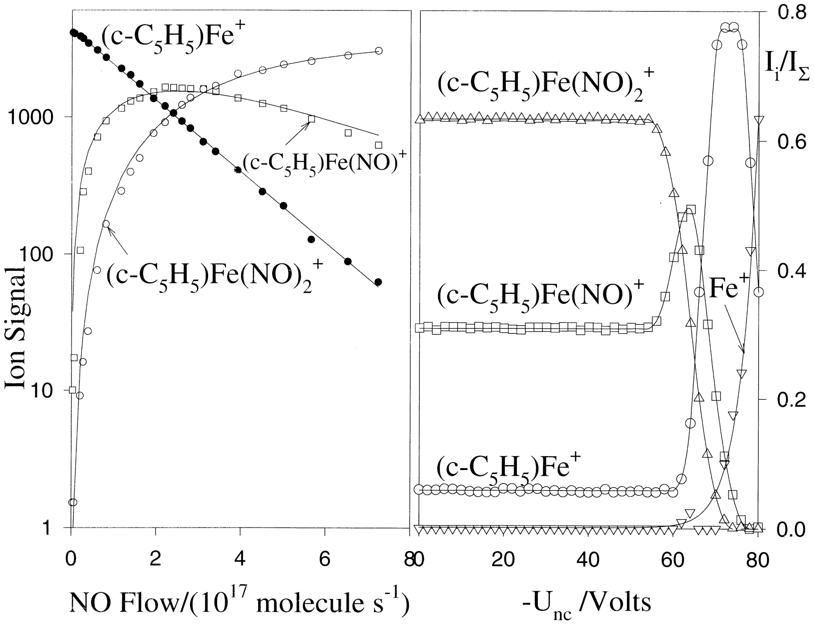


Fig. 3. (Left) Experimental data for the reaction of (c-C_5H_5)Fe^+ with NO. The measurements were performed at 294 ± 3 K and at a helium buffer-gas pressure of (0.35 ± 0.01) Torr. The solid lines represent a fit of the experimental data with the solution of the differential equations appropriate to the observed sequential reactions. (Right) Multi-CID results for (c-C_5H_5)Fe$(NO)_n^+$ in the laboratory energy scale and a flow of NO = 5.0×10^{17} molecules s^{-1}.

We have reported previously that H_2, N_2, and CO_2 do not react measurably with the bare Fe^+ cation under similar operating conditions, $k < 1 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}, and that N_2O reacts slowly with Fe^+ to oxidize iron and produce FeO^+ with $k = 3.1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} [22]. The measurable occurrence of ligation in the presence of the c-C_5H_5 ligand can be attributed largely to an enhanced lifetime of the intermediate complex due to the enhanced number of degrees of freedom that can be effective in energy dispersal [17]. The rate of ligation with N_2 [14] and N_2O [15] is enhanced by a factor of $>10^3$ and ~10, respectively, in helium bath gas at 0.35 Torr. We have reported elsewhere that the presence of C_6H_6 as a ligand enhances the rate of ligation with N_2 by a factor of 1.5×10^3 and that C_2H_4, C_6H_6, and C_{60} as ligands also enhance considerably (by more than a factor of 4) the reactivity of Fe^+ with N_2O, although the bulk of that increase is accounted for by an increase in the branching ratio of the oxidation channel. It is also of interest to note that we did not observe the oxidation of (c-C_5H_5)Fe^+ by N_2O, although we did observe previously a slow oxidation reaction with Fe^+. Apparently the oxidation channel with (c-C_5H_5)Fe^+ is preempted by the collisional stabilization of the ligated adduct.

3.2. Reactions with NO and CO

More than one sequential addition was observed in the ligation of (c-C_5H_5)Fe^+ by CO and NO. Fig. 3 shows experimental data for the sequential addition of two NO molecules according to

$$(c\text{-}C_5H_5)Fe(NO)_n^+ + NO + He \rightarrow (c\text{-}C_5H_5)Fe(NO)_{n+1}^+ + He \qquad (4)$$

and Fig. 4 shows the addition of three CO molecules according to

$$(c\text{-}C_5H_5)Fe(CO)_n^+ + CO + He \rightarrow (c\text{-}C_5H_5)Fe(CO)_{n+1}^+ + He \qquad (5)$$

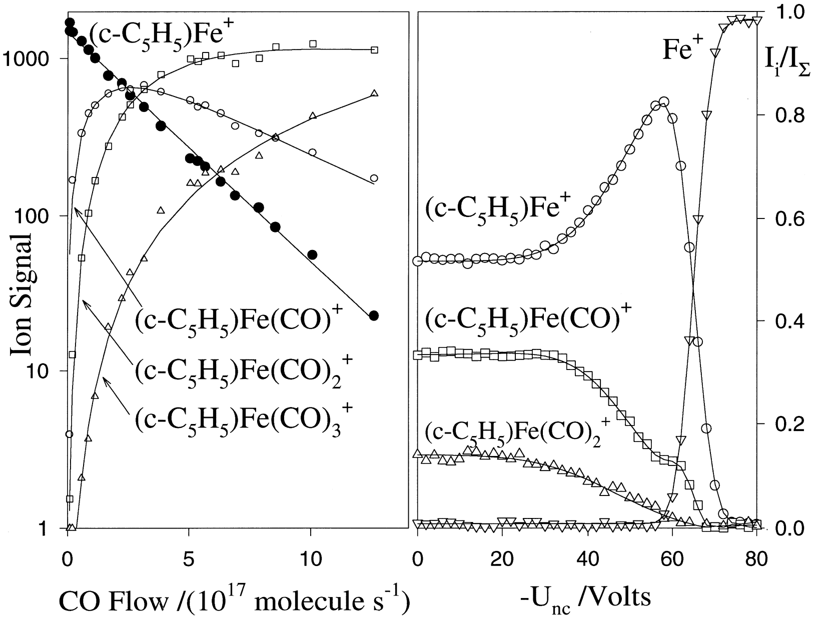


Fig. 4. (Left) Experimental data for the reaction of (c-C_5H_5)Fe^+ with CO. The measurements were performed at 294 ± 3 K and at a helium buffer-gas pressure of 0.35 ± 0.01 Torr. The solid lines represent a fit of the experimental data with the solution of the differential equations. (Right) Multi-CID results for (c-C_5H_5)$Fe(CO)_n^+$ in the laboratory energy scale and a flow of CO = 1.8×10^{17} molecules s^{-1}.

There was no evidence for further ligation. The first two additions are quite rapid in each case, $k \sim 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}.

The CID profiles shown in Fig. 3 indicate that the two NO ligands are bonded with similar energies. Fig. 4 suggests somewhat weaker bonding with the first two CO ligands. Also, the structure in the (c-C_5H_5)$Fe(CO)^+$ profile suggest that two isomers of (c-C_5H_5)$Fe(CO)^+$ may be formed with slightly different ligation energies, perhaps due to different orientations of the CO molecule, viz. (c-C_5H_5)$Fe(CO)^+$ and (c-C_5H_5)$Fe(OC)^+$.

We have reported previously that NO and CO do not react measurably with the bare Fe^+ cation under similar operating conditions, $k < 1 \times 10^{-11}$ and $k < 1 \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1}, respectively. Again, we attribute the measurable occurrence of ligation in the presence of the c-C_5H_5 ligand to an enhanced lifetime of the intermediate complex. Ligation of Fe^+ with c-C_5H_5 enhances the rate of ligation with CO by a factor of 10^4. This is consistent with our previous observation of an enhancement by more than 5×10^3 of the rate of ligation in the presence of C_2H_4, C_6H_6, and C_{60} as ligands [15].

3.3. Reactions with H_2O and NH_3

Water and ammonia are unique among the ligands investigated here in the sense that these molecules have the capacity for hydrogen bonding in an outer coordination shell. We have reported previously the results of our measurements of the kinetics of ligation of (c-C_5H_5)Fe^+ with ammonia [16]. Up to three ammonia molecules were observed to add sequentially (see rate coefficients in Table 1) and the CID profile of (c-C_5H_5)$Fe(NH_3)_3^+$ showed two populations that are consistent with the occurrence of hydrogen bonding of the third ammonia ligand in a fraction of the (c-C_5H_5)$Fe(NH_3)_3^+$ ions.

The observed sequential chemistry initiated by (c-C_5H_5)Fe^+ with H_2O is shown in Fig. 5. This chemistry can be described by the sequential ligation of the following reactions:

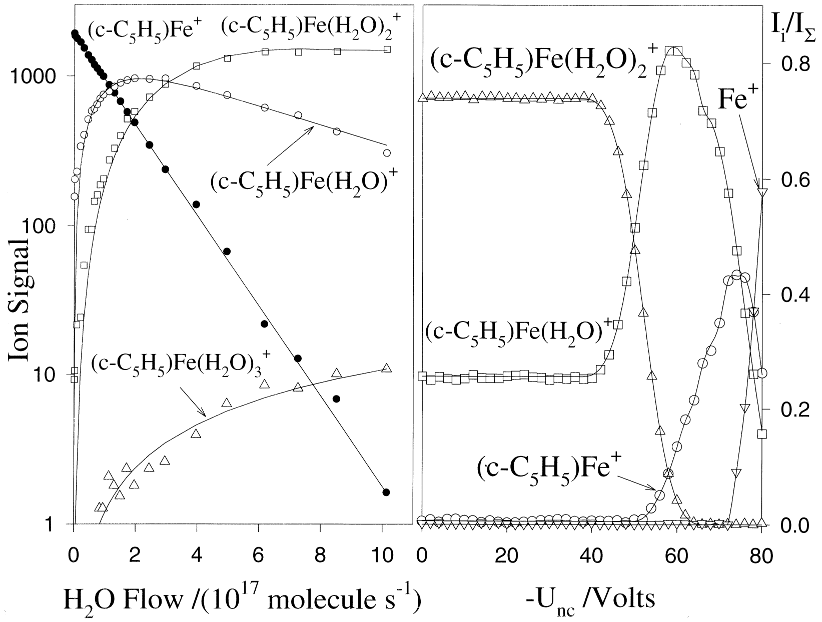


Fig. 5. (Left) Experimental data for the reaction of $(c\text{-}C_5H_5)Fe^+$ with H_2O. The measurements were performed at 294 ± 3 K and at a helium buffer-gas pressure of 0.35 ± 0.01 Torr. The solid lines represent a fit of the experimental data with the solution of the differential equations appropriate to the observed sequential reactions. (Right) Multi-CID results for $(c\text{-}C_5H_5)Fe(H_2O)_n^+$ in the laboratory energy scale and a flow of $H_2O = 7.3 \times 10^{17}$ molecules s^{-1}.

$$(c\text{-}C_5H_5)Fe^+ + H_2O + He \rightarrow (c\text{-}C_5H_5)Fe(H_2O)^+ + He \quad (6)$$

$$(c\text{-}C_5H_5)Fe(H_2O)^+ + H_2O + He \rightarrow (c\text{-}C_5H_5)Fe(H_2O)_2^+ + He \quad (7)$$

$$(c\text{-}C_5H_5)Fe(H_2O)_2^+ + H_2O + He \rightarrow (c\text{-}C_5H_5)Fe(H_2O)_3^+ + He \quad (8)$$

for which the effective bimolecular rate coefficients are summarized in Table 1. The rate of ligation drops with increasing ligation slowly at first for the addition of the second water molecule, by a factor of about 3, and rather precipitously, by a factor of about 30, for the addition of the third water molecule. The addition of a fourth water molecule was not observed in the range of water additions employed. Ligation of bare Fe^+ by water was not observed in our earlier measurements, $k < 10^{-13}$ cm^3 molecule^{-1} s^{-1} [22], so that in this case ligation with $c\text{-}C_5H_5$ has increased the reactivity of Fe^+ by a factor of at least 10^4.

3.4. Reaction with NO_2

Fig. 6 shows that $(c\text{-}C_5H_5)Fe^+$ reacts rapidly with NO_2, $k = 4.5 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, in two distinctly different ways. The main branch (85%) leads to the oxidation of iron by O-atom transfer according to

$$(c\text{-}C_5H_5)Fe^+ + NO_2 \rightarrow (c\text{-}C_5H_5)FeO^+ + NO \quad (9a)$$

but this channel competes (15%) with direct ligation,

$$\rightarrow (c\text{-}C_5H_5)Fe(NO_2)^+ \quad (9b)$$

The main oxidation channel (9a) is analogous to the oxidation of the unligated Fe^+ that we have observed previously and proceeds with a similar efficiency under similar conditions [22].

The CID profiles in Fig. 6 are consistent with two types of dissociation: $(c\text{-}C_5H_5)FeO^+$ dissociation to produce FeO^+ at relatively low voltages (~ −50 V), apparently followed by the dissociation of FeO^+ itself to produce the early rise in Fe^+ and the dissociation of $(c\text{-}C_5H_5)Fe^+$ at higher voltages to produce more Fe^+.

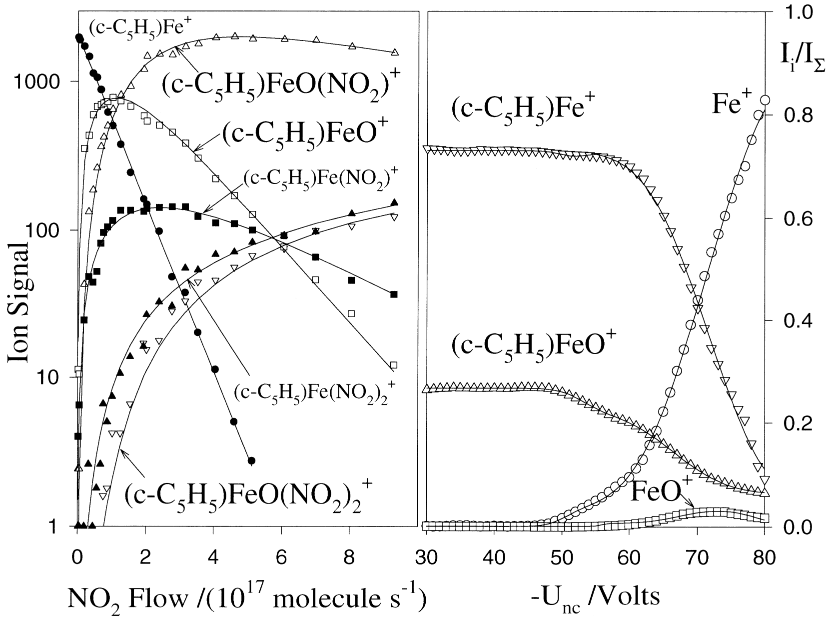


Fig. 6. (Left) Experimental data for the reaction of (c-C_5H_5)Mg^+ with NO_2 in helium buffer gas at 294 ± 3 K and 0.35 ± 0.01 Torr. (c-C_5H_5)Mg^+ was produced initially by 25 eV electron impact dissociative ionization of magnesocene vapour. The solid lines represent a fit of the experimental data with the solution of the differential equations appropriate to the observed sequential reactions. (Right) Multi-CID results for (c-C_5H_5)$Mg(NO_2)_n^+$ in the laboratory energy scale and a flow of $NO_2 = 2.7 \times 10^{16}$ molecules s^{-1}.

3.5. Variation in the rate of ligation with the number of ligands

Fig. 7 provides an overview of the ligation kinetics observed with the inorganic ligands investigated. The measured values for the apparent bimolecular rate coefficients for ligation with a single molecule at room temperature range from 3.6×10^{-13} to 1.6×10^{-9} cm^3 $molecules^{-1}$ sec^{-1} for H_2 and NH_3, respectively. Ligation efficiencies taken as the ratios k_{exp}/k_c (see Table 1) range from 0.0024 to 1.0 for H_2 and H_2O, respectively. These correlate roughly with the strength of the (c-C_5H_5)Fe^+/ligand interaction. Also the number of ligands observed to add sequentially ranges from 1 to 3. Only one addition was observed in the ligation of (c-C_5H_5)Fe^+ by H_2, N_2, CO_2, and N_2O. Two additions were observed with NO and NO_2 and three with CO, H_2O, and NH_3. Except in the case of H_2O and NH_3, these numbers should correspond to the intrinsic coordination numbers for (c-C_5H_5)Fe^+. The situation with H_2O and NH_3 is different since both of these molecules either may bond directly to the Fe center in an inner coordination sphere or may bond in an outer coordination sphere by weaker hydrogen bonding already after the addition of the first ligand. Concurrent “innershell” ligation and “outershell” ligation could also occur and this would obfuscate the determination of primary coordination numbers. We have previously shown that with ammonia the measured CID profiles indicate a competition between direct ligation and hydrogen bonding for the addition of the third NH_3 molecule [16]. The third adduct was not sufficiently intense to allow a similar CID study with water. But it is clear from the data that the coordination number for (c-C_5H_5)Fe^+ is ≥2 with both ammonia and water.

3.6. Structures and bonding in ligated (c-C_5H_5)FeL^+

Open from one hemisphere, the ion metal center in (c-C_5H_5)Fe^+ is readily accessible to approaching ligands. The mode of coordination can be expected to depend on the electronic properties of the metal center

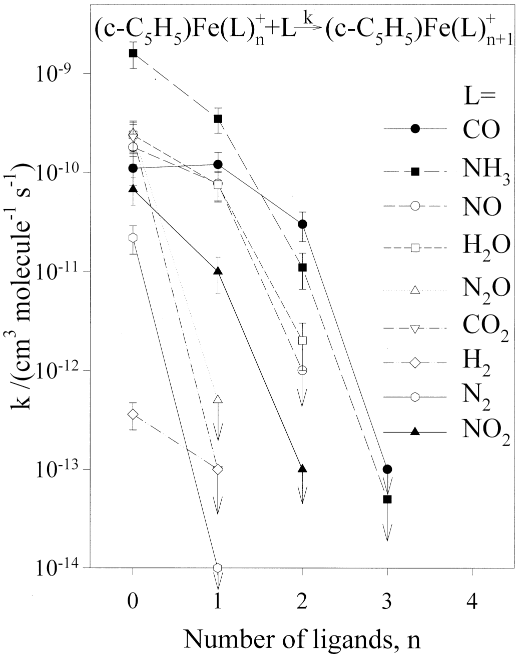
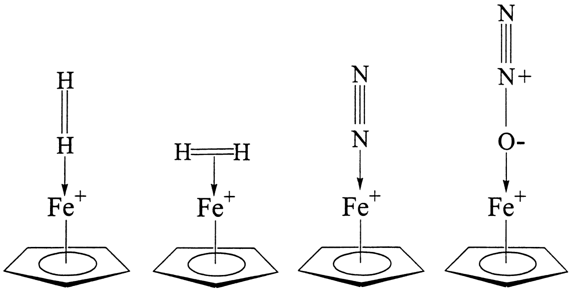


Fig. 7. A semilogarithmic correlation of the rate coefficient for the sequential ligation of $(c\text{-}C_5H_5)Fe^+$ by H_2, N_2, CO, CO_2, NO, NO_2, N_2O, H_2O, and NH_3 with the number of ligands, *n*, added in the gas phase at 294 ± 3 K and at a helium buffer-gas pressurum buffer gas at a total pressure of 0.35 ± 0.01 Torr; reaction[a] and collision[b] rate coefficients are given in units of cm^3 $molecules^{-1}$ s^{-1}

and the steric and electronic properties of the ligand. The ground-electronic state of $(c\text{-}C_5H_5)Fe^+$ ($^5E_2$) [9] has been characterized theoretically, together with its binding energy (77 ± 10 kcal mol^{-1}) which compares favorably with the experimental values of 88 ± 7 [12]. The threshold for dissociation observed in our CID experiments is consistent with such a high bond energy. The bonding in the $^5E_2$ ground state can be comprehended in terms of electron transfer from Fe^+ to the $c\text{-}C_5H_5$ ligand to form $(c\text{-}C_5H_5)^-Fe^{2+}$ and back donation from the six π electrons in $(c\text{-}C_5H_5)^-$ to primary 4*s* and 4*p* orbitals of Fe^{2+}. Such bonding should leave only one orbital available for further bonding with another ligand without changing multiplicity. It is likely that weak ligands such as H_2, N_2, N_2O, and CO_2 will not change the multiplicity of $(c\text{-}C_5H_5)Fe^+$. In contrast, CO, NO, N_2O, H_2O, and NH_3 apparently reduce the resulting complex multiplicity and ligate more than once with Fe in the $(c\text{-}C_5H_5)Fe^+$ ion.

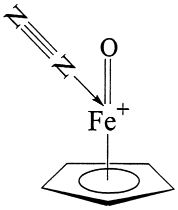


Scheme 1.

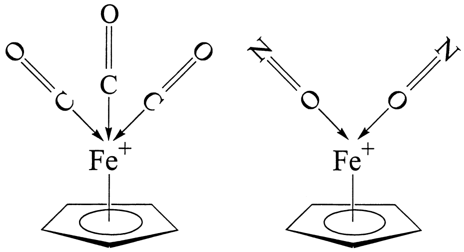
Weak ligands can be classified according to the type of bonding to the transition metal as: σ-bond electron pair (H_2) and lone pair (N_2, N_2O) donating ligands. Interest in σ-bond electron-pair donating ligands is related to classical/nonclassical behavior in the complex [23–25]. Bonding in these complexes can be over three centers [Fe–(η^2-H_2)], which weakens but does not break the H–H bond, or conventional two-center (an oxidative addition) leading to H–H bond breaking.

Iron in $(c\text{-}C_5H_5)FeL^+$ is too weak, as a Lewis acid, to transform these bonds into the conventional 2*e*, two-center bonds. However, it is a much better π base in bonding over three (as can be proposed in the case of H_2 addition) or over two centers [$(c\text{-}C_5H_5)Fe(\eta^1\text{-}N_2)^+$ and $(c\text{-}C_5H_5)Fe(\eta^1\text{-}N_2O)^+$]. There are two different binding modes of dinitrogen as a ligand: η^1 and η^2. For metal–dinitrogen complexes end-on η^1 is most common, although η^2 side-on bonding by way of dinitrogen π bonds is also known [26–31]. For N_2 ligation the $(c\text{-}C_5H_5)Fe(\eta^2\text{-}N_2)^+$ bonding is unlikely but still possible. Our CID results showed no evidence for oxidative addition. For example, dissociation of the ligated ions $(c\text{-}C_5H_5)Fe(H_2)^+$, $(c\text{-}C_5H_5)Fe(N_2)^+$, and $(c\text{-}C_5H_5)Fe(N_2O)^+$ did not show H, N, or N_2/O elimination, respectively. No evidence for bond insertion was observed. Some possible modes of ligation that are consistent with our experimental observations are illustrated in Scheme 1.

The absence of O-atom abstraction in reaction (1) in the case of the N_2O ligand is perhaps surprising



Scheme 2.



Scheme 3.

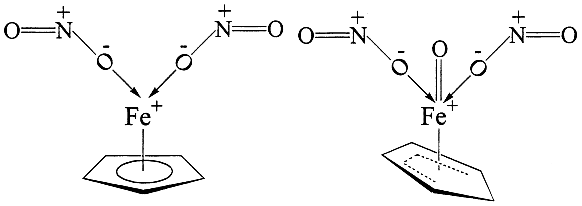
since the O-atom affinity of N_2 is quite low, 40 kcal mol^{-1} [32]. This may be attributed to the unfavorable increase in the formal oxidation number of iron up to 4 that would be required in the formation of the $(c\text{-}C_5H_5)Fe^+$–O bond [15]. However, the $(c\text{-}C_5H_5)FeO^+$ ion is obtained in reaction with NO_2 although NO is thermodynamically less favorable as a leaving group than dinitrogen. For $(c\text{-}C_5H_5)Fe^+$ quite strong ligand fields are required to cause spin pairing. It seems that N_2O is too weak as a ligand to overcome the spin reduction barrier so that the oxidation channel is pre-emptied by the collisional stabilization of the ligated complex. Such barriers have been suggested previously for reactions of high-spin bare metal ions with N_2O [33]. NO_2 is a strong ligand–radical and the oxidation channel predominates, but, even in this case, ligation by NO_2 is also observed as a (minor) competing channel.

In comparison with $(c\text{-}C_5H_5)Fe^+$, FeO^+ reacts slower with N_2O and sequentially forms ligand adducts from $FeO(N_2O)^+$ to $FeO(N_2O)_3^+$ with effective bimolecular rate coefficients of 1.1, 1.1, and 1.4×10^{-11} cm^3 $molecule^{-1}$ s^{-1}, respectively [15]. These rate coefficients are relatively small and so are more consistent with weak ligand-bond formation. The failure of $(c\text{-}C_5H_5)Fe(N_2O)^+$, for which we presume C_{5v} symmetry $[(c\text{-}C_5H_5)Fe(\eta^1\text{-}N_2O)^+]$, to add another ligand ($k < 5 \times 10^{-13}$) cannot then be attributed to the resulting closed electron shell of iron and most probably is related to a low energy of secondary N_2O binding, which is not enough for the complex spin reduction. As a speculation, such a behavior of $(c\text{-}C_5H_5)Fe(N_2O)^+$ can point toward Scheme 2 for the adduct observed.

Iron in $(c\text{-}C_5H_5)FeO^+$ is almost coordinatively saturated by cyclopentadienyl ligand from one side and by oxygen from the other. $(c\text{-}C_5H_5)FeO(\eta^1\text{-}N_2)^+$ is consistent with the Tolman's 18-electron rule [34], but our CID experiments showed no evidence for this mode of coordination.

As in the case of CO ligation in which the carbonyl donates two electrons to the metal center, NO is expected to form a linear Fe–NO connectivity in which the nitrosyl ligand can be considered as a 2*e* donor cation NO^+ (isoelectronic with CO) that transfers its odd electron to the metal and so acts as a 3*e* donor. This is consistent with the higher onset energy for the collision-induced removal of the NO ligand compared to the CO ligand. We report in this study that the $(c\text{-}C_5H_5)Fe^+$ cation as a strong p base readily reacts with three carbonyl and two nitrosyl groups to complete its valence shell and so becomes coordinatively saturated. Possible $(c\text{-}C_5H_5)Fe^+$–ligand connectivities are indicated in Scheme 3.

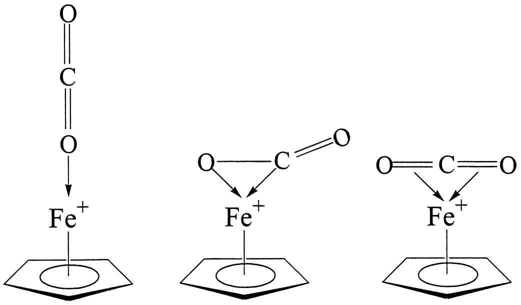
The interaction between $(c\text{-}C_5H_5)Fe^+$ cation and NO_2 neutral molecule leads to the formation of $(c\text{-}C_5H_5)FeO^+$ in 85% of all primary reaction events. There are two filled $p\pi$ orbitals on the oxygen atom which can interact with appropriately directed $d\pi$ orbitals on the iron atom and make the metal atom strongly deactivated for metal–ligand bonding from the oxygen hemisphere. A previous attempt in our laboratory to investigate the coordination properties of iron in iron oxide cation [22] showed that there is free access to the metal for neutral inorganic ligands only from the side of the iron atom. In the case of $(c\text{-}C_5H_5)FeO^+$ the iron is almost coordinatively saturated by cyclopentadienyl ligand from one side and by oxygen from the other. Also, FeO^+ was seen to react fast with NO_2 in a bimolecular fashion to produce NO^+ and O^+ can be realized as a result of



Scheme 4.

strong dipole–dipole interaction, viz. there is a stabilizing electrostatic interaction between the positive charge of the iron bonded to oxygen and cyclopentadienyl and the negative charge of the oxygen atom of the nitrogen dioxide. The response of the cation to the coordination of NO_2 may be a slight bending of the ring and braking fivefold symmetry of $(c\text{-}C_5H_5)FeO^+$ (see Scheme 4) [35,36].

There are several coordination modes of binding of carbon dioxide to a metal [37]. Both the steric and electronic properties of the co-ligands affect the stability of the carbon dioxide–metal complexes. The η^2 mode [38] has been shown to be present in several metal complexes in the solid state and in solution $[(c\text{-}C_5H_5)_2Mo(CO_2)$ [39]. The formal η^1-C mode [40], the μ^2-O, μ^1-C, η^3-form [41] have been well established too. To date the η^1-O mode has not been isolated but this mode of binding has been postulated to exist at 14 K in some adducts of carbon dioxide [42]. These data were acquired from solid state studies, mostly performed through x-ray diffraction and from very few studies in solution [43]. In solution at room temperature, carbon dioxide is fluxional with an intermolecular motion (rotation) that involves η^1-C or η^1-O intermediates. An important question arises: does carbon dioxide maintain similar modes of binding in the gas phase? Unfortunately, our experiment presents only indirect evidence for assignment of the $(c\text{-}C_5H_5)Fe(CO_2)^+$ structure. We assume that for $(c\text{-}C_5H_5)Fe^+$ ion in the gas phase the η^1-O mode is preferable as an intermediate because of the high local negative charge present on oxygen atoms in CO_2, and this is due to the parent ion being much more electropositive than is coordinated iron in solid or ionized in solution and partly shielded by solvent molecules. We expect that under SIFT experimental conditions an unimolecular rearrangement reaction and successive collision stabilization lead to the formation of the η^2 mode σ complex. For this reaction where the ligand contains π electrons, we have also proposed the structure of the species connected in an allene like π complex (see Scheme 5) [22]. In these cases carbon dioxide acts as a bidentate ligand, and the first adduct is the most stable product for this reaction in the gas phase.



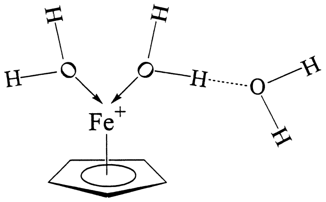
Scheme 5.

The tendency to fill the valence shell of transition metal forces the $(c\text{-}C_5H_5)Fe(CO_2)^+$ complex to attach another carbon dioxide, presumably in the η^1 mode, while our experiments show that the latter can not be observed. Previous investigations in our laboratory [22] have demonstrated the formation of three sequential addition complexes in the case of iron oxide cation, and for bare iron ion no association was observed. Steric limitations due to repulsion by a previously ligated group and the weakness of CO_2 as a ligand are possible explanations for the absence of $(c\text{-}C_5H_5)Fe(CO_2)_2^+$ formation in our experiment.

The adduct ions $(c\text{-}C_5H_5)Fe(H_2O)_n^+$, where $n = 1$ and 2, can be expected to have water ligands to be attached to the iron in the η^1-O mode. The binding of any additional water molecules is much slower and probably involves hydrogen binding in a second coordination shell as is illustrated in Scheme 6 for $(c\text{-}C_5H_5)Fe(H_2O)_3^+$.

3.7. Ligation energetics

The thermochemical tabulation reported by Lias et al. [44] indicates a standard enthalpy change for



Scheme 6.

disassembling the ferrocene ion into Fe^+ and two $C_5H_5^{\cdot}$ radicals of 184 kcal mol^{-1}. This is consistent, within experimental uncertainties, with the results of photodissociation experiments with gas-phase ferrocene cations that lead to $C_5H_5^{\cdot}$ elimination and have provided a value for $D[(c\text{-}C_5H_5)Fe^+\text{–}(c\text{-}C_5H_5)]$ of 85 ± 7 kcal mol^{-1} [45] and the results of CID experiments that have provided a value for $D[(c\text{-}C_5H_5)\text{-}Fe^+]$ of 88 ± 7 kcal mol^{-1} [12]. Our failure to observe ligand-switching reactions in our room-temperature measurements with either $(c\text{-}C_5H_5)_2Fe^+$ or $(c\text{-}C_5H_5)Fe^+$ indicates that the ferrocene and cyclopentadienyliron cations have the highest Fe–L bonding energies of all the ligated species observed in the experiments reported here, viz. $D[(c\text{-}C_5H_5)Fe^+\text{–}L] < 85 \pm 7$ kcal mol^{-1} and $D(Fe^+\text{–}L) < 88 \pm 7$ kcal mol^{-1} for $X = H_2$, H_2O, NH_3, CO, N_2, NO, CO_2, N_2O, and NO_2. Also, our failure to observe the production of FeL^+ in the multi-CID experiments with the mixed ligated species of the type $(c\text{-}C_5H_5)FeL^+$ indicate that the $(c\text{-}C_5H_5)Fe^+\text{–}L$ bond is the weakest bond in these species.

The appropriate qualitative approach to understanding the $(c\text{-}C_5H_5)Fe^+\text{–}L$ multi-CID results reported here is to consider the relative $(c\text{-}C_5H_5)Fe^+\text{–}L$ bond strength as the only insight which can be extracted from these experiments [18]. To this end, when the product ion appearance energy is used as a measure of the multi-CID threshold, $D[(c\text{-}C_5H_5)Fe^+\text{–}H_2] < D[(c\text{-}C_5H_5)Fe^+\text{–}N_2] < D[(c\text{-}C_5H_5)Fe^+\text{–}N_2O] < D[(c\text{-}C_5H_5)Fe^+\text{–}CO_2] \approx D[(c\text{-}C_5H_5)Fe^+\text{–}(CO)] < D[(c\text{-}C_5H_5)Fe^+\text{–}H_2O] < D[(c\text{-}C_5H_5)Fe^+\text{–}NO] < D[(c\text{-}C_5H_5)Fe^+\text{–}NH_3] < D[(c\text{-}C_5H_5)\text{–}Fe^+]$ of 88 ± 7 kcal mol^{-1}.

4. Conclusions

Reactivities have been measured for the cyclopentadienyliron cation $(c\text{-}C_5H_5)Fe^+$ with the inorganic ligands H_2, H_2O, CO, N_2, NO, O_2, CO_2, N_2O, and NO_2 at 294 ± 2 K in helium buffer gas at a total pressure of 0.35 ± 0.01 Torr. The full sandwich ferrocene cation $(c\text{-}C_5H_5)Fe^+$ was found to be unreactive with these ligands. The measurements provide intrinsic efficiencies and intrinsic coordination numbers for the ligation of the $(c\text{-}C_5H_5)Fe^+$ cation at room temperature. These were both observed to be sensitive to the nature of the ligand. Only addition was observed with all but one of these ligands: with NO_2 oxygen-atom transfer was the dominant reaction channel. There was no evidence for secondary adduct formation for $L = H_2$, N_2, N_2O, and CO_2 or the oxidation of iron. In contrast, multiple ligation of the $(c\text{-}C_5H_5)Fe^+$ cation was observed with NO, NO_2, CO, H_2O, and NH_3. Some insight into ligation energetics is provided by the failure of ligand switching reactions and by the onset of multicollision-induced dissociation. A number of the ligated species have been observed for the first time.

Acknowledgements

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