

Intramolecular Translocation of a Nitrogen Atom from a Nitrosyl to a Cyclopentadienyl Ligand of $(C_5H_5)_2Fe_2NO^+$ As Probed by Neutralization Reionization Mass Spectrometry

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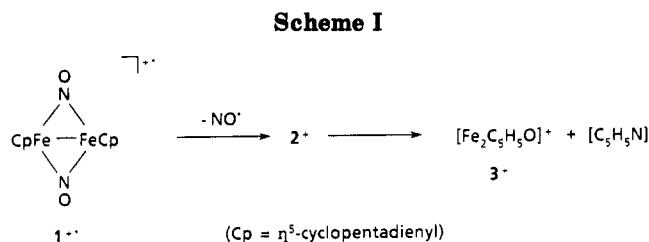
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Summary: Dimeric cyclopentadienyliron nitrosyl is studied by tandem mass spectrometry, including the technique of neutralization reionization mass spectrometry (NRMS). From the cationic binuclear cluster $(C_5H_5)_2Fe_2(NO)^+$ unimolecular loss of C_5H_5N is observed, and by means of NRMS the neutral C_5H_5N is unequivocally characterized as pyridine. For the corresponding ionic product both collisional activation and NRMS point to the formation of a cyclopentadienyl diironoxide cation. In addition, the neutral binuclear cluster $(C_5H_5)_2Fe_2O$ is also shown to exist as a viable molecule in the gas phase. A mechanism for the unusual nitrogen atom insertion in a cyclopentadienyl ligand of an organometallic compound is suggested.

Nitrogen monoxide $NO^•$ is a versatile ligand in organometallic chemistry,¹ especially for its different binding modes to mono- and oligonuclear organometallic compounds. Of particular importance are the η^1 -end-on and the bridging coordination of $NO^•$.² Most recently, it was reported that $NO^•$ plays an important role as a human neural transmitter, with iron-centered enzymes acting as receptors in those processes.³

In addition to serve as an open-shell ligand, the metal-promoted cleavage of the nitrogen-oxygen bond in $NO^•$ was observed in the condensed phase.^{4a-d} This process can be viewed as a model for the catalytic degradation of nitrous oxides, which is important with respect to the role of nitrogen monoxide in atmospheric chemistry.^{4e} Activation of $NO^•$ has also been reported to occur in the gas-phase ion chemistry of metal clusters.⁵ One of the most intriguing examples concerns the oxidation of carbon monoxide to carbon dioxide by the cationic cluster Co_2NO^+ in the course of which the nitride Co_2N^+ is formed.^{5b}

In earlier gas-phase organometallic ion chemistry studies a unique type of reaction was reported for several mono-



and dinuclear transition metal nitrosyl complexes.^{6,7} During fragmentation of ions containing LM(NO) units the nitrosyl nitrogen atom is transferred to the free-radical moiety L with migration of the nitrosyl oxygen atom to the central metal M. These processes, which are accompanied by the corresponding metastable peaks, seem to be restricted to ions with an even number of electrons. Examples have been reported for L = μ -NO (loss of N_2O), μ -NH₂ (loss of N_2H_2), η^5 -cyclopentadienyl (loss of C_5H_5N), and σ -phenyl (loss of C_6H_5N). Unfortunately, the mass spectrometric techniques available at that time did not permit the unraveling of the structural and mechanistic features of these remarkable intramolecular nitrogen atom transfer processes.

In this paper, we report the results of a more refined study of this rearrangement by application of advanced tandem mass spectrometry to dimeric cyclopentadienyliron nitrosyl, $(C_5H_5)_2Fe_2(NO)_2$, 1. In the electron impact mass spectrum of 1 a metastable peak corresponding to the formal elimination of $[C_5H_5N]$ from $[1 - NO^•]^+$, 2⁺, was observed (Scheme I).⁶ Because of the very high abundance of the product ion $C_5H_5Fe_2O^+$, 3⁺, in the 70-eV mass spectrum, 1 appeared to be a good candidate for this study. In particular, the technique of neutralization-reionization mass spectrometry⁸ is shown once more to serve as a valuable tool to unequivocally prove composition of neutrals lost and of ions formed from organometallic complexes in the gas phase which may afford structural information of such species.⁹

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Table I. Mass Differences in the Unimolecular (MI) and Collision-Induced (CA) Fragmentations of 1⁺, 2⁺, and 3⁺ (Data Are Given in % Relative to the Base Peak)^a

Δm	ion	1 ⁺		2 ⁺		3 ⁺	
		MI	CA	MI	CA	MI	CA
2	H ₂					7	3
18	H ₂ O			18	6	8	8
26	C ₂ H ₂					100	100
28	CO					45	17
30	NO [•]	100	100	7	7		<i>b</i>
31	HNO				12		<i>b</i>
40	C ₃ H ₄					9	22
56	Fe					2	9
60	2 NO [•]		<1				
61	NO [•] + HNO		5				
65	C ₅ H ₅ ⁺				1		75
72	FeO					4	7
79	C ₅ H ₅ N			100	100		
86	FeNO			1	18		
109	C ₅ H ₅ N + NO		8			7	75
116	[FeN ₂ O ₂]	2	6				

^a Some of the mass differences can also be assigned to other elemental compositions of the neutrals (e.g., $\Delta m = 28$ is either CO or C₂H₄). ^b $\Delta m = 30$ and 31 correspond to consecutive hydrogen losses after C₂H₂ and CO loss, respectively, and are formed in small amounts each (3 and 1%, respectively).

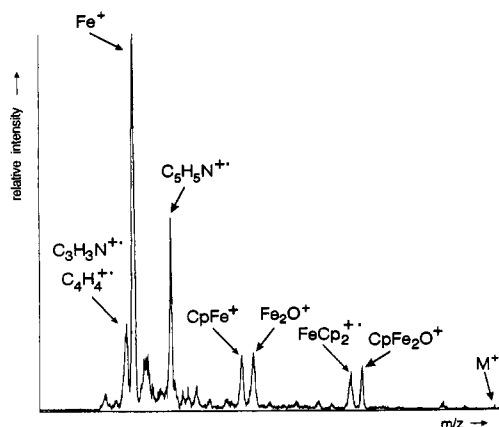


Figure 1. Neutralization reionization mass spectrum (NRMS) of 2⁺ (xenon, 85%/oxygen, 85%).

Experimental Section

The experiments were performed with a modified VG ZAB/HF/AMD four sector mass spectrometer of BEBE configuration (B stands for magnetic and E for electric sector), which has been described previously.¹⁰ Briefly, 1 was admitted to the ion source via the solid probe inlet system. In order to obtain maximal ion currents of 1⁺, the temperature in the range 80–160 °C was raised with a rate of ca. 5 °C/min. Ionization was achieved by a beam of electrons having 70 eV kinetic energy in an electron impact ion source (repeller voltage ca. 20 V). The ions were accelerated to 8 keV translational energy and the species of interest, containing the ⁵⁶Fe isotope only, mass-selected by means of B(1) and E(1) at a resolution of $m/\Delta m = 3.000$. Unimolecular fragmentations occurring in the field-free region preceding the second magnet were recorded by scanning B(2); the so-obtained spectra will be referred to as MI-spectra. For collisional activation (CA) experiments, the mass-selected ions were collided with helium (80% transmission, this corresponds on average to 1.1–1.2 collisions¹¹). The fourth sector of the instrument was not used in the present study. For NRMS experiments, the precursor ions were mass-selected by means of B(1) and subjected to a double-collision experiment. Neutralization was performed by

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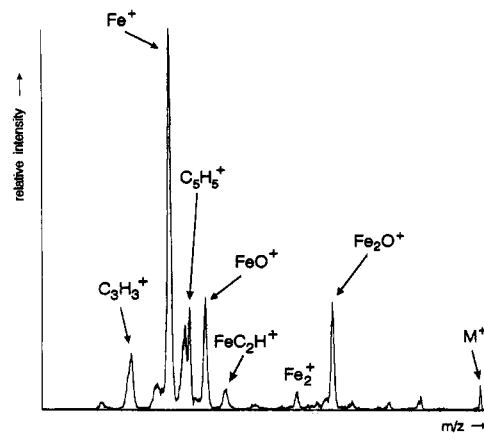
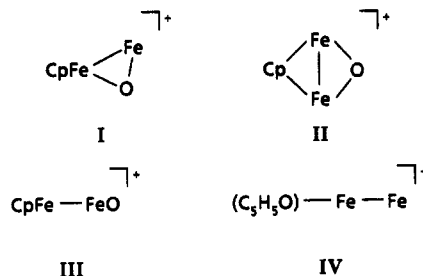


Figure 2. NRMS of 3⁺ (the same conditions as described in Figure 1).

Chart I



collision with xenon (85% transmission), and the remaining ions were deflected by charging a deflector electrode to 1000 V; the beam of fast neutrals was subsequently reionized by collision with oxygen (85% transmission), and the so-formed ions were analyzed by scanning E(1). The relatively low vapor pressure of 1 made it necessary to perform the NRMS experiments with the first two sectors only at a mass resolution of $m/\Delta m \approx 2.000$.

All spectra were accumulated and on-line processed with either the VG 250/11 or the AMD-Intectra data system; 5–40 scans were averaged to improve the signal-to-noise ratio.

1 was synthesized according to the literature¹² and purified by recrystallization from toluene.

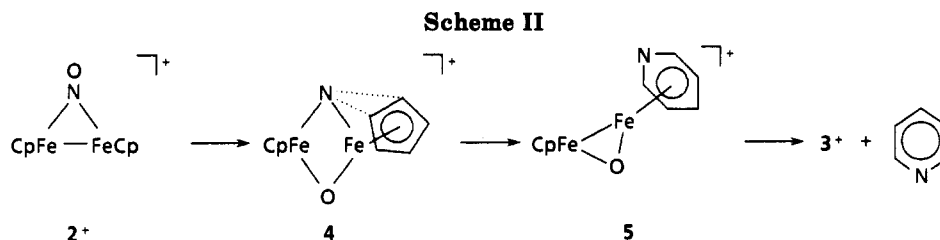
Results and Discussion

The MI spectrum of 1⁺ is dominated by the loss of one NO ligand (Table I). In addition, the ferrocene radical cation is formed in small amounts; this fragmentation pathway increases upon collisional activation. Formally, the latter reaction corresponds to the loss of neutral [FeN₂O₂] from 1⁺; however, consecutive losses of NO[•] and FeNO are also feasible (vide infra).¹³ The other fragments formed upon collisional activation of 1⁺ are basically derived from that of 2⁺. Note that a signal due to the losses of 2NO is hardly observed in the CA mass spectrum of 1⁺ (<1%).

For mass-selected 2⁺ three unimolecular fragmentations are of relevance: (i) elimination of a water molecule, (ii) loss of a second NO[•], leading to the dicyclopentadienyl diiron cation, and (iii) formation of [Fe₂C₅H₅O]⁺, 3⁺, and neutral [C₅H₅N]. The latter process gives rise to the base peak. With respect to the CA spectrum of 2⁺ two distinct features are remarkable: (i) in addition to the loss of NO[•]

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a neutral nitroxyl molecule HNO is formed preferentially,¹⁴ and (ii) the ferrocene radical cation is generated in surprisingly high yield (18%).⁷ The latter finding not only implies that ferrocene is formed from 1^{++} by consecutive losses of NO^\bullet and FeNO but also that the Fe-Fe interaction in 2^+ is weak as compared to other ionic iron clusters.¹⁵

With regard to the unimolecular reactivity of 2^+ , the central question concerns the nature of $[\text{C}_5\text{H}_5\text{N}]$: Does the mass difference $\Delta m = 79$ correspond to an intact entity formed by a nitrogen atom insertion in the cyclopentadienyl unit, or are separate fragments formed, e.g., $\text{C}_5\text{H}_5^\bullet$ and N^\bullet ? To this end, 2^+ was subjected to an NRMS experiment.^{9e,17} A recovery signal, corresponding to reionized 2 , is hardly observed in the NR spectrum (Figure 1). This finding is in line with previous examples, in which metal complexes with noncovalently bound ligands were reported not to give rise to intense recovery signals.^{9e,19} Interestingly, the base peak of the NR spectrum corresponds to bare Fe^+ . Since collision-induced fragmentation in the neutralization step is unlikely when xenon is used,²⁰ Fe^+ has to originate either from dissociation of neutral 2 or is produced by dissociative reionization of 2 and neutral fragments formed thereof. The second iron atom in 2 remains in the ligand sphere and gives rise to the ferrocene radical cation and its characteristic fragment $\text{Fe}(\text{C}_5\text{H}_5)^+$; both signals are present in the NR spectrum.²¹ The intense signal for reionized $\text{C}_5\text{H}_5\text{N}^{++}$ unambiguously confirms the presence of this molecule as an intact entity. The relatively high intensity of the radical cation as compared to its fragments, the characteristic HCN and C_2H_2 losses (giving rise to $\text{C}_4\text{H}_4^{++}$ and $\text{C}_3\text{H}_3\text{N}^{++}$, respectively), and thermodynamic considerations¹⁶ clearly suggest that pyridine has been formed. In addition, the ratio of fragment ions generated in a NRMS experiment of authentic Fe-(pyridine)⁺ is practically identical with that reported in Figure 1. Our assignment is further supported by the observation of the complementary signal for $[\text{Fe}_2\text{C}_5\text{H}_5\text{O}]^+$.

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(21) The formation of ferrocene by thermolysis of neutral 1 has also been observed (ref 6).

Next we will address the structure of 3^+ , which is formed by the loss of pyridine from 2^+ . Most likely, a cyclopentadienyl- μ -oxidodiiron cation, I, is formed in the course of the reaction; however, other structures are also chemically conceivable, i.e., II-IV (Chart I). For several reasons the MI as well as the CA spectra of 3^+ do not allow a clear-cut structure assignment for this ion: (i) In the unimolecular dissociation of 3^+ the relatively abundant losses of molecular hydrogen, water, and—most probably—carbon monoxide indicate substantial structure-unspecific rearrangement processes involving the cyclopentadienyl ligand in 3^+ . Although the formations of the unsaturated hydrocarbon neutrals C_2H_2 and C_3H_4 are typical for an intact cyclopentadienyl moiety, they do not permit a distinction between I-III. (ii) Both the cyclopentadienyl radical loss from 3^+ as well as the elimination of neutral FeO are unusual unimolecular processes and may be attributed to "hot" 3^+ . (iii) Although the intensities of the fragments derived from rearrangement processes decrease significantly upon collisional activation, an unambiguous structure assignment remains impossible.

However, in the NR mass spectrum of 3^+ three characteristic features can be distinguished: (i) The observation of a recovery signal for 3^+ establishes that neutral 3 is a viable molecule within the time frame of the experiment (ca. 10 μs). In view of the results of previous studies,^{9,19} this finding indicates that the ligands as well as the metal atoms in 3 are bounded covalently. (ii) Intense signals corresponding to Fe_2O^+ , Fe_2^+ , FeO^+ , and Fe^+ establish the existence of a diironoxide moiety in 3 , with the oxygen atom being most likely bound as a bridging ligand. The relative intensities of these fragments are in agreement with known thermochemical data of Fe_2O .^{15d,16} (iii) The fragment corresponding to reionized $\text{C}_5\text{H}_5^\bullet$ demonstrates that 3 contains an intact cyclopentadienyl group, thus ruling out structure IV. Other signals present in the NR spectrum are either derived from the C_2H_2 and C_3H_4 losses from 3 or due to consecutive fragmentations of the ions discussed above. Any evidence for an attachment or insertion of the oxygen atom in the carbon skeleton of the cyclopentadienyl is absent. On the basis of these findings and the thermochemical stabilities of analogous systems^{15d} only structures I and II are in keeping with the present data.

In conclusion, the present results suggest the following possible mechanism for the N-atom insertion in the cyclopentadienyl ligand of 2^+ : In the first step ($2^+ \rightarrow 4$) the bridging NO ligand in 2^+ is split to form compound 4. A similar mechanism was suggested for the cleavage of NO^\bullet by cationic cobalt clusters in the gas phase.⁵ The dotted lines in structure 4 are meant to indicate an interaction of the free valencies of the N atom with a double bond of a cyclopentadienyl ligand. 4 may eventually isomerize to 5 from which the pyridine ligand is liberated to form 3^+ (presumably present as I or II). Alternatively, nitrogen atom insertion in the Cp ring and N-O bond cleavage may occur simultaneously. As a test for this

mechanism we propose the investigation of the corresponding trinuclear complexes. In these compounds the attractive interaction of the N atom and a C-C double bond should be largely reduced by the presence of a third metal atom; consequently, the nitrogen atom translocation should be less prominent or not take place at all.

We are currently exploring further reactions of nitrogen monoxide with transition metal cluster ions, which might also serve as model systems for the activation of molecular

nitrogen. Obviously, these and related studies will profit from the potential of NRMS to structurally characterize ionic and neutral organometallic compounds.

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