INTERACTIONS OF IRON DINITROSYL COMPOUNDS WITH IMIDAZOLE AND ITS DERIVATIVES

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TITLE: INTERACTIONS OF IRON DINITROSYL COMPOUNDS WITH IMIDAZOLE AND ITS DERIVATIVES

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ABSTRACT

Nitric oxide has been implicated in a number of biological processes, the majority of them involving iron nitrosyl complexes. The urgency then is to further study and characterize these complexes to further the understanding of biological mechanisms. However, the chemical sensitivity of these species precludes the purification and isolation of these compounds which, unfortunately, has directed the trend to merely detecting the presence of these compounds rather than isolating them. To this day, a large number of Electron Paramagnetic Resonance (EPR) detectable, biological compounds have not been isolated.

To this end, the series of biologically relevant compounds of the form $Fe(NO)_2(L)_2$ [L = imidazole **1**, 1-methylimidazole (1-MeIm) **2**, 4-methylimidazole (4-MeIm) **3**, benzimidazole (benzim) **4**, and 5,6-dimethylbenzimidazole (56benzim) **5**] have been synthesized by direct reaction of the appropriate imidazole ligand with $Fe(NO)_2(CO)_2$. The compounds were extremely air sensitive, both in solution and as a dry solid. This hindered attempts to purify these compounds and so, infra red (IR), nuclear magnetic resonance (NMR) and EPR spectroscopic studies were undertaken of 2:1 reaction mixtures of the appropriate imidazole ligand and $Fe(NO)_2(CO)_2$. These studies revealed that the rapid substitution of the carbonyl ligands is facilitated by a catalytic, 17-electron, electron transfer chain mechanism (ETC), where the imidazole ligand acts to oxidize the 18-electron complex into the active 17-electron $Fe(NO)_2(CO)_2^+$ species.

In the course of the EPR study of **2**, crystals formed that were suitable for single-crystal, X-ray diffraction. The compound crystallizes with a monoclinic unit cell, in the C2/c

space group with unit cell dimensions: a = 13.985(5) Å, b = 11.529 (5) Å, c = 15.471(4) Å, $\alpha = 90°$, $\beta = 91.72(2)°$, $\gamma = 90°$, V = 2493(2) $Å^3$, Z = 8. During the course of study of **6**, crystals suitable for single crystal X-ray diffraction were obtained. The compound crystalizes with a monoclinic unit cell, in the P2/c space group and unit cell dimensions: a = 11.707(9) Å, b = 8.1783 (5) Å, c = 17.2489 (13) Å, $\alpha = 90°$, $\beta = 106.562$ (1)°, $\gamma = 90°$, V = 1583.0 (2) $Å^3$, Z = 2.

A relatively new mass spectrometry (MS) procedure was utilized for the reaction mixtures of **1** - **5**, which involved a combination of electrochemical oxidation and electrospray. The method proved very useful, yielding data that could not be obtained by other MS techniques. Oligomeric species of the form L-[$(Fe(NO)_2L]_x$ (x = 2,3,4,5 or 6), were also detected by MS for each compound reaction mixture. The oligomers involved linear chains of iron dinitrosyl fragments linked via the imidazole nitrogens. However, it is believed that these oligomers are produced as a result of the conditions met by the mass spectrometer.

A reaction of $Fe(NO)_2(PPh_3)(CO)$ with 1-MeIm was also performed in hopes of producing a more stable mono-substituted complex. However, the reaction also proceeded via an Electron Transfer Chain (ETC) pathway to produce $Fe(NO)_2(PPh_3)_2$ **6**.

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1. Introduction

It is well known that the earth's atmosphere functions as a an insulating, thermal barrier, much like a greenhouse, and in doing so, provides the warmth necessary for the persistence of life on earth. The destruction of the "natural" protective atmosphere arises from four sources a) increased production of greenhouse gases such as the type of formula NO_x, b) increase in acidity of natural rain by nitrogen and sulfur oxides, c) depletion of the protective ozone layer by radical nitrogen oxide species, d) increased levels of secondary pollutants such as peroxyacetyl nitrate (PAN). Figure 1.1 shows the cycle that gives rise to

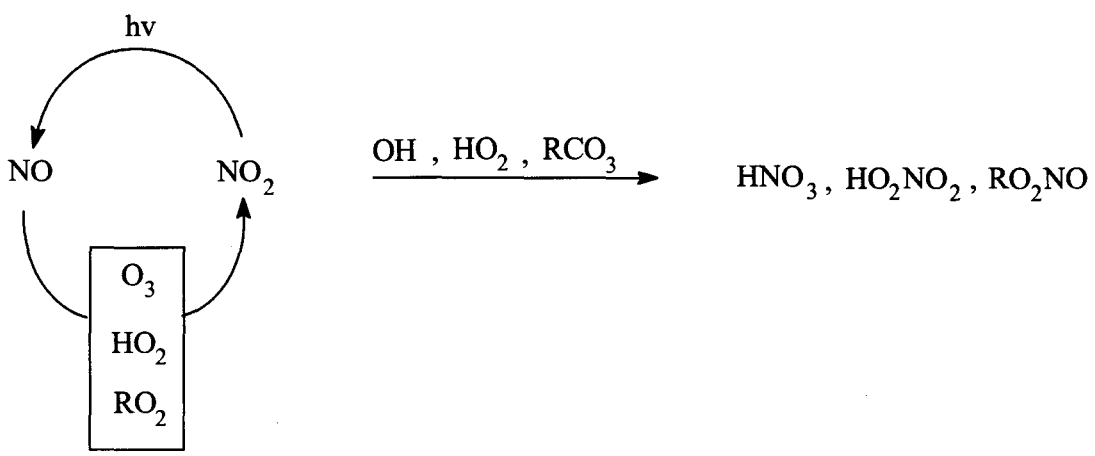


Figure 1.1. The NO/NO_2 removal processes in the troposphere

these concerns with regards to NO_x in the troposphere.

Naturally occurring nitrogen oxides (NO_x) originate from forest regions, marshlands, and grasslands. Other "natural" sources of NO_x are derived from forest fires, and lightning where the temperature may reach upwards of 30,000 K.[1] Nearly all of the anthropogenic

NO_x production occurs as a result of high temperature combustion devices, *via* the oxidation of N_2 or organic nitrogen compounds. Indeed, it is the brown colour of gaseous NO_2 that helps contribute to haze associated with smog-induced low visibility in industrialized cities.

The nitric oxide gases are known to cause respiratory problems, while PAN causes eye irritation. Nitrogen dioxide (NO_2) initiates lipid oxidation in biological systems, and its inhalation has been associated with the biosynthesis of carcinogenic nitrosamines. Also, nitrogen oxides have been found to stimulate the nitration of polycyclic aromatic hydrocarbons *in vivo* to produce complexes that display mutagenicity, genotoxicity and carcinogenicity.[2]

However, despite the increasing environmental concern over nitric oxide gases and toxicological health issues, the nitric oxide (NO) molecule has been found to be one of the most important biological molecules ever discovered and has recently been named molecule of the decade.[3] This discovery has lead researchers to aggressively pursue the little known life of NO in living systems.

1.2 The Role of Nitric Oxide in Living Systems

The biological activity related to nitric oxide can be divided into two areas, indirect and direct effects. The principal reason that the chemical biology of NO can be partitioned in this manner is because NO has the capacity to react with molecules either directly, or as a pre-formed derivative or a metal complex.

1.2.1 Indirect effects of NO

The association of NO with stimulation of cyclic guanosine monophosphate (cGMP) production consequently links NO with a variety of physiological effects.[4] Cyclic GMP can act directly on ion channels and activate protein kinases, which catalyse the phosphorylation or dephosphorylation of proteins.[4] Furthermore, cyclic GMP directly regulates membrane cation channels in retinal photoreceptor cells, mediates smooth muscle relaxation, inhibits platelet aggregation, modulates excretion of Na^+ by the kidney, and helps to regulate cardiac function by modulating Ca^{2+} currents.[5] Sodium nitroprusside, $Na_2[NO(CN)_5Fe]\cdot 2H_2O$, which has been marketed as Nipride,[5] is often used to lower blood pressure in humans. Its hypotensive effect is evident within seconds after infusion, and the desired blood pressure is usually obtained in 1-2 minutes. Other nitrosyl compounds such as $K[NOBr_5Ir]$, $K_2[NOCl_5Ru]$ and $[NO(NH_3)_5Ru]Cl_3$ have also shown vasodilatory activity, presumably by releasing NO, but are too toxic for clinical use.

NO plays an important role as a messenger between neurons at synapses in the central nervous system,[3] where it acts as a diffusable, short lived molecule within a local space to help shape the three dimensional network of synaptic responses. It now appears that NO, functioning as a neuromodulator in the hippocampus of the brain plays a fundamental role in the basic neuronal processes that initiate learning and experience.[4]

Nitric oxide is produced by macrophages to kill both invasive cells and in the rejection of tissue grafts.[5] The toxic effect appears to come from inhibition of enzyme activity through nitric oxide bonding to non-heme iron-centers in proteins such as ribonucleotide reductase, and release of intracellular iron from the cells targeted by the

macrophages.

1.2.2 Direct Effects of NO

Nitric oxide exists as a persistent, stable radical. However, NO does not rapidly react with most biological substances in a manner analogous to oxygen radicals such as ·OH. Since the lifetime of NO *in vivo* is relatively short (less than 10 sec) only the faster direct reaction of NO, such as with metal centers or other radicals, proves to be important. Reactions with metal centers, mainly iron, are crucial to understanding the bioregulatory behaviour of NO.

Another important direct reaction of metal centers with NO is seen with cytochrome P450. Studies have shown the NO inhibits mammalian P450, which is thought to regulate hormone metabolism and, under infectious conditions, decrease drug metabolism in the liver. The inhibitory mechanism relies on formation of an Fe-NO bond formation which prevents the binding of oxygen, similar to the mechanism for CO inhibition.

Metalloproteins play a major role in controlling concentrations of nitric oxide *in vivo*. Nitric oxide reacts directly with oxyhemoglobin (HbO_2) or oxymyoglobin to form nitrate and methemoglobin (MetHb) or metmyoglobin,[6] which reduces the intracellular concentrations of NO.

The reaction of heme proteins with NO is also important to understanding the mechanism for protection against reactive species in the body. Peroxides are thought to enter a cell and react with heme proteins to form ferryl (Fe=O) heme complexes. The ferryl heme

protein is then proposed to decompose and generate superoxide anion $O_2^{-\cdot}$ and release the iron complex. The iron complex can further react with peroxides to generate very potent oxidants such as $HO_2\cdot$ and H_2O_2. NO reacts with the iron complex, which results in the formation of methemoglobin[6] and inhibits the formation of oxidants.

One of the first clues that the immune system utilizes NO to combat pathogens came from electron paramagnetic resonance (EPR) studies in cells showing the formation of $Cys_2Fe(NO)_2$.[7] It has been proposed that NO may react directly with ferrodoxin proteins such as aconitase, an enzyme containing a 4Fe-4S cluster that catalyses the isomerization of citrate to isocitrate in the citric acid cycle, destroying the iron-sulfur cluster which results in the loss of enzymatic activity.

1.3 Structure and Bonding in Metal Nitrosyl Complexes

The bonding in transition metal carbonyl or nitrosyl complexes may be considered to be made up of two components: (a) donation of electron density from a σ-type orbital on CO or NO onto the metal, and (b) a donation of electron density from the occupied metal *d*-orbitals into the π^* antibonding orbitals of the NO or CO ligand. The bonding picture described in Figure 1.2 applies to both nitrosyl and carbonyl bonding interactions. However, there are significant differences in the nature of the electron distributions in the M-NO and M-CO units. One difference stems from the fact that the nitrogen of NO is more electronegative than the carbon of CO,[8] the result being that the NO ligand is a better overall electron acceptor than CO. Another important difference is that in the M-NO unit, the M-N

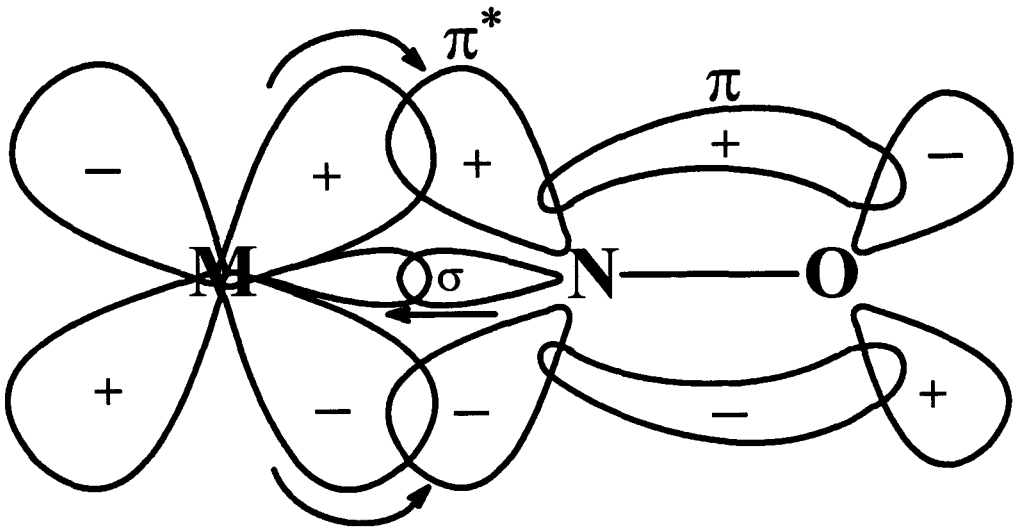


Figure 1.2. Molecular Bonding diagram for Metal Nitrosyls

bond is usually strong, and the N-O bond is relatively weak; for carbonyls, the reverse trend is observed. The end result is that the M-N bond is strengthened and shortened by the back-donation while the addition of electron density to the antibonding π^* orbital weakens and lengthens the NO bond. In general, NO is considered to be a weak σ-donor and a strong π-acceptor.

The nitrosyl group can bond to transition metals in a variety of ways, resulting in different geometries about the N atom. One method used to describe the bonding of nitrosyl compounds (the method used in this thesis) is to assign formal oxidation states to the metal and the nitrosyl ligand.[8] With this assignment, a linear M-NO (Figure 1.3 A) unit would occur as the result of a bound NO^+ ligand (which is isoelectronic with CO and N_2). Coordination of nitric oxide as NO^+ involves a net donation of three electrons from NO to a metal atom. The extra electron is considered to be in the *d* set of orbitals of iron, giving rise to an oxidation state of -2 for $Fe(NO)_2(L)_2$ complexes. A bent M-NO (Figure 1.3 B) unit would be the result of a bound NO^- ligand. Coordination as NO^- involves a net donation of

one electron to the metal.

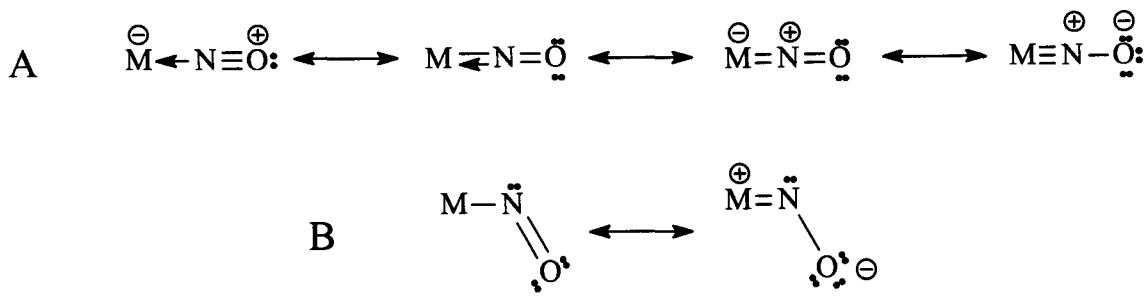


Figure 1.3. Nitrosyl Bending in Metal complexes. A: Linear "3 electron" bonding. B: Bent "1 electron bonding"

1.4 The Chemistry of Metal Nitrosyl Complexes

1.4.1 Formation of Metal Nitrosyls

There are a number of ways in which iron nitrosyl complexes are prepared. The earlier syntheses involved the combination of aqueous solutions of Fe(II) salts, anionic ligands and a source of NO gas.[9] These methods produced useful EPR results, but the shortcoming of this earlier work was that isolation and purification of the compounds was not accomplished.

The most successful formation of metal nitrosyl complexes is by displacement of ligands in the coordination sphere of a metal. Again, this can be accomplished by using NO gas to displace a ligand equivalent to that of a 3-electron donor.[10] Nitric oxide gas can also displace two-electron ligands in some monometallic compounds, with subsequent formation of a bimetallic species (presumably because of the extra electron afforded by NO); it can also add to a bi- or polymetallic complex with the subsequent cleavage of metal-metal bonds.[11]

Nitrosonium salts have also been used for the synthesis of metal nitrosyls. NO^+ forms simple 1:1 adducts with some coordinatively unsaturated metal complexes (Equation 1).[12]

$$Ir(CO)ClL_2 + NO^+ \rightarrow [Ir(NO)(CO)ClL_2]^+ \quad (1)$$

NO^+ also readily displaces CO (or other 2-electron ligands such as carbon disulfide) in a number of coordinatively saturated complexes to generate their nitrosyl analogues (eq 2, 3),[12]

$$CpMn(CO)_3 + NO^+ \rightarrow [CpMn(NO)(CO)_2]^+ + CO \quad (2)$$

$$Fe(CO)_2(PPh_3)_2(CS_2) + NO^+ \rightarrow [Fe(CO)_2(PPh_3)_2NO]^+ + CS_2 \quad (3)$$

and a variety of nitrosyl halides have been used extensively in formation of metal complexes.[13]

Inorganic nitrites have also been used to obtain metal nitrosyl complexes. The most common nitrite sources for the synthesis of monometallic and cluster complexes are $PPN(NO)_2$ and sodium nitrite (eq 4, 5).

$$Cr(CO)_6 + PPN(NO_2) \rightarrow PPN[Cr(NO)(CO)_4] \quad (4)$$

$$Ru(CO)_5 + PPN(NO_2) \rightarrow PPN[Ru(NO)(CO)_3] \quad (5)$$

The fact that, in acidic media, the nitrite ion equilibrates with the NO^+ cation has been exploited (6) for nitrosylation (7, 8).

$$NO_2^- + 2H^+ \leftrightarrows H_2O + NO^+ \quad (6)$$

$$[Ru(bipy)_2(H_2O)Cl]^+ + NO_2^- \rightarrow \text{No reaction} \quad (7)$$

$$[Ru(bipy)_2(H_2O)Cl]^+ + NO_2^-/H^+ \rightarrow [Ru(NO)(bipy)_2Cl]^{2+} \quad (8)$$

Other metal nitrosylation reactions have been accomplished by reactions with azides, organic nitroso ligands, hydroxylamine and protonation of aminato-type ligands.[12]

1.4.2 The Reactivity of Metal Nitrosyls

The M-NO moiety exhibits a wide range of reactivity, including simple conformational changes and reactions at the N and O atoms. In simplistically viewing the linear NO ligand as an electrophile (formally NO^+), it should be rendered prone to nucleophilic attack at the nitrosyl nitrogen. Conversely, the bent NO ligand (formally NO^-) should undergo electrophilic attack at the nitrogen atom. The NO groups can also serve as "spectator" ligands, while still conferring unique chemical reactivity to metal centers.

In solution, a number of compounds have shown the ability to convert from linear to bent conformations. For example, the five coordinate $[RuCl(NO)_2(PPh_3)_2]BF_4$ complex possesses both linear and bent ligands in the solid state but is fluxional in solution due to a rapid, intramolecular interconversion.[14]

The compound $[Ir(NO)(\eta^3\text{-}C_3H_5)(PPh_3)_2]^+$ (Figure 1.4) in solution also shows a linear-bent NO interchange,[15] in the absence of interchange occurs without an accompanying η^3-η^1 allyl fluxional process. Both linear and bent nitrosyl forms of the complex have been crystallized as their PF_6^- and BF_4^- salts.

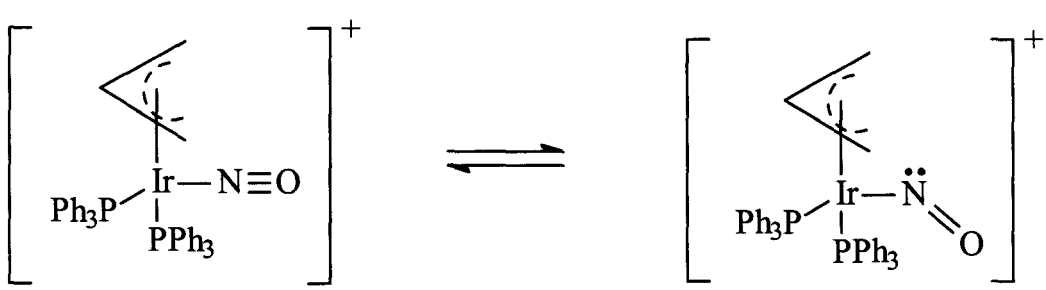


Figure 1.4 Linear-bent interchange of $[Ir(NO)(\eta^3\text{-}C_3H_5)(PPh_3)_2]^+$.

The linear-to-bent NO conformational changes may be induced chemically by the

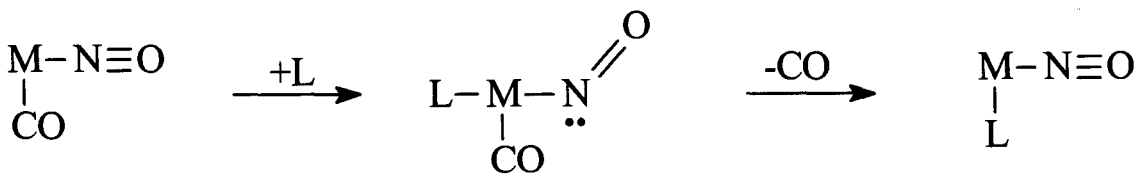


Figure 1.5. Linear-bent interchange by chemical addition.

addition of neutral or anionic nucleophiles (L) to the metal center as shown in Figure 1.5. For example, $[Co(NO)(das)_2]^{2+}$ (das = O-phenlyenebis(dimethyl)arsine) has a linear (179°) nitrosyl. Addition of thiocyanide to this complex gives rise to $[Co(NO)(das)_2(NCS)]^{2+}$ with a bent nitrosyl (132°).[16]

Lewis acids such as $AlMe_3$, Cp_3Er and Cp_3Yb can react with the oxygen of nitrosyls, forming the corresponding adducts.[17,18] When the Lewis acid binds with the nitrosyl oxygen, electron density is drained away from the NO group, and the metal compensates by donating more electron density into the π^* orbitals of NO. Thus, the ν_{NO} is lowered, by an amount determined by the strength of the interaction between the NO ligand and the lewis acid.

The oxygen of the NO ligand can also be removed by oxygen acceptors (eq 9).[19]

$$[FeRu_3(NO)(CO)_{12}]^- \longrightarrow [FeRu_3(N)(CO)_{12}]^- + CO_2 \quad (9$$

If the MNO group is sufficiently electron rich, it may undergo electrophilic attack by protons. The bent NO is formally sp^2 hybridized and possesses a lone pair of electrons (eq 10, 11).[20]

$$Os(NO)Cl(CO)(PPh_3)_2 + HCl \rightarrow Os(HNO)Cl_2(CO)(PPh_3)_2 \quad (10)$$

$$Re(NO)_2(PPh_3)_2(I) + HCl \rightarrow Re(NO)(HNO)(PPh_3)_2Cl(I) \quad (11)$$

Nucleophiles can react with the nitrogen of NO if the M-NO unit is essentially linear. It has been proposed [21] that addition of hydride anion to $[CpRe(NO)(CO)(PPh_3)]^+$ results in the formation of a formyl complex *via* an HNO intermediate, which isomerizes to the formyl product as shown in Figure 1.6.

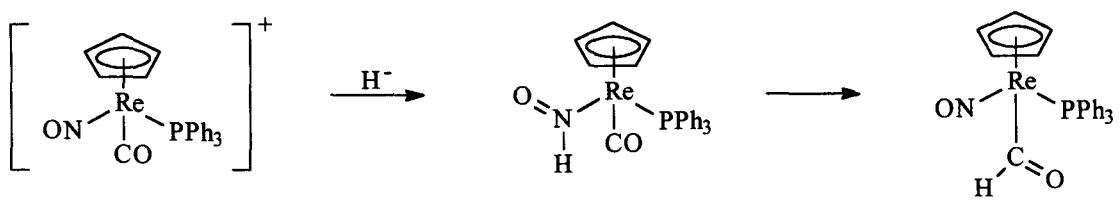


Figure 1.6. Reaction of a nucleophile with the nitrogen of NO.

Similarly, the reaction of a cobalt dinitrosyl complex with borohydride leads to reduction of the NO ligand and the formation of ammonia (12).[22]

$$[Co(NO)_2(PPh_3)_2 \xrightarrow{BH_4^-} Co(NO)(PPh_3)_3 + NH_3 \quad \textbf{(12)}$$

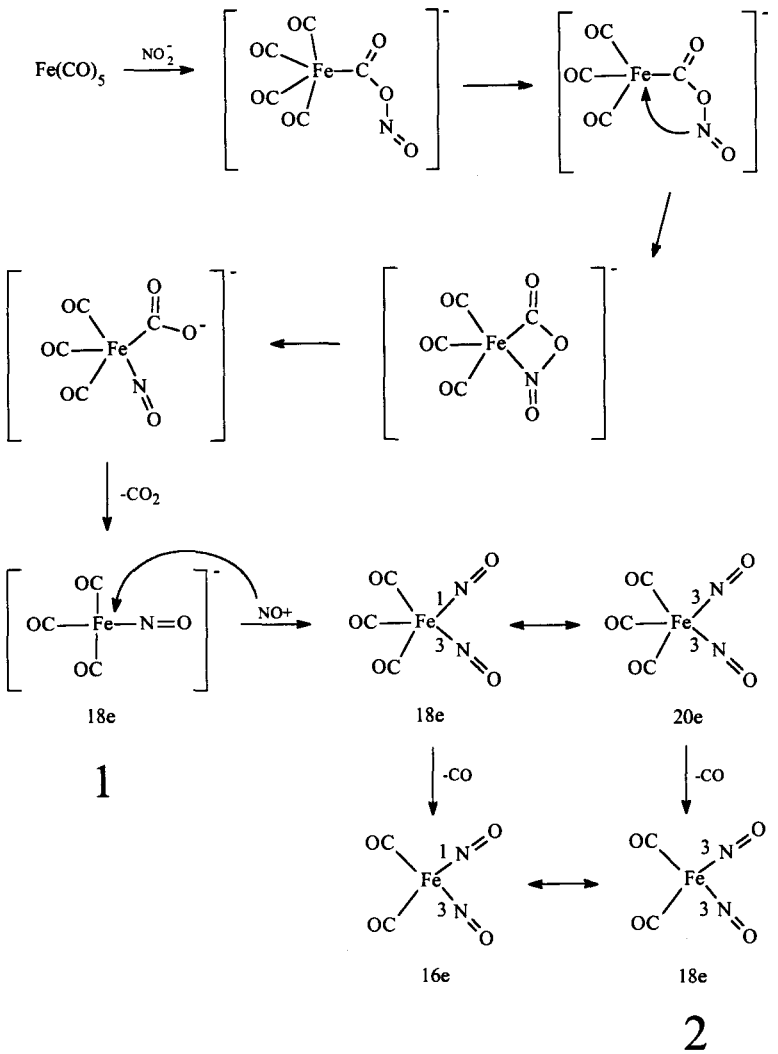
1.4.3 Irondinitrosyldicarbonyl

The formation of a volatile iron nitrosyl-carbonyl was first observed by Mond and Wallis.[23] It is a deep red compound, with a melting point of 18.4 °C and a density of 1.56g.cm^{-3}. $Fe(NO)_2(CO)_2$ is diamagnetic, having a filled d^{10} shell. It is insoluble in water but

very soluble in organic solvents. The liquid starts decomposing at 50 °C,[24] leading to Fe_2O_3 and other products. $Fe(NO)_2(CO)_2$ is unstable in air and decomposes slowly at room temperature by oxidation. With NaOH or $NaOCH_3$ in CH_3OH disproportionation of Fe occurs yielding $[Fe(CO)_3NO]^-$ and $[Fe(CH_3OH)_5NO]^{2+}$, CO and NO^-. The Formation of $Fe(NO)_2(CO)_2$ by $Fe(CO)_5$ and nitrite is shown in Scheme 1.1. The reaction takes place initially in methanol. At step **1** in the scheme, $Na[Fe(CO)_3NO]$ is formed. The methanol is distilled off and the salt dried, at which point water and more nitrite is added to the salt, and the resulting slurry is acidified with CO_2 to produce the starting material **2** in the scheme.

The geometry of the iron centre is reflected in the nature of the ligands attached.[25] For example, the $Fe(NO)_2$ unit has a large angle for N-Fe-N. The configuration develops because a better π overlap between the Fe and N orbitals is achieved at wider angles. In general, strong π-acids (L) will necessarily have a large L-Fe-L angle. Conversely, the much weakerπ-acids, such as Cl-, will have a smaller L-Fe-L angle. The poor π-acceptors rely mainly on σ interactions, which operate at more acute angles. The geometry can also be reflected in the electronic configuration of the iron center. The oxidation of the d^{10} $Fe(NO)_2$ complex to d^9 causes geometric distortions,[26] involving a change in shape from tetrahedral to more of a trigonal pyramid, with a missing ligand at the apex. The single electron is occupied in the d_z^2 orbital, which pushes the ligands down. The change from d^9 to d^8 further distorts the four coordinate complex towards a square planar conformation.[25] The $Fe(NO)_2(L)_2$ [L = PR_3, NR_3] compounds formed by reaction of $Fe(NO)_2(CO)_2$ and L have been shown to proceed by a conventional associative mechanism.[27] The conventional process is slow, requiring stirring overnight to replace the first carbonyl and requiring

heating at 85 °C overnight to replace the second carbonyl.[28] A number of $Fe(NO)_2(X)_2$ [X



Scheme 1.1. Proposed mechanism of formation of $Fe(NO)_2(CO)_2$.

= PR_3,][29]and $[Fe(NO)_2(CO)]_2Y$ [Y = dppe or dppm[30]] compounds have been previously synthesized, and the ortep diagrams of $[Fe(NO)_2(CO)]_2$dppe and dppm are shown in Figures 1.7 and 1.8, respectively. Each iron is situated in a pseudo-tetrahedral environment.

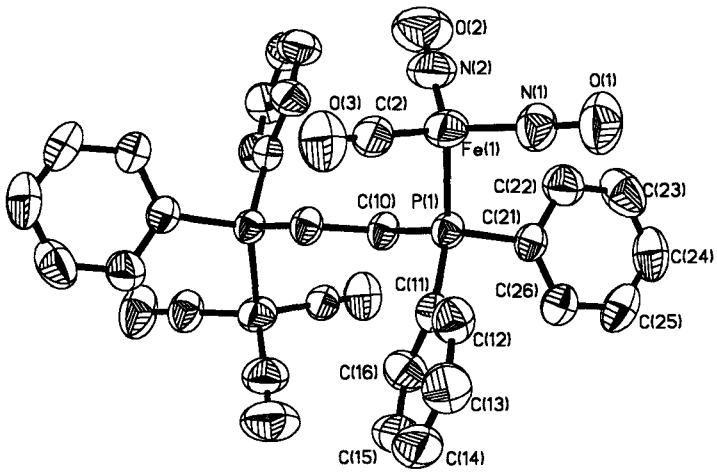


Figure 1.7. Ortep diagram of $[Fe(NO)_2(CO)]_2dppe$, shown with 50% thermal ellipsoids.

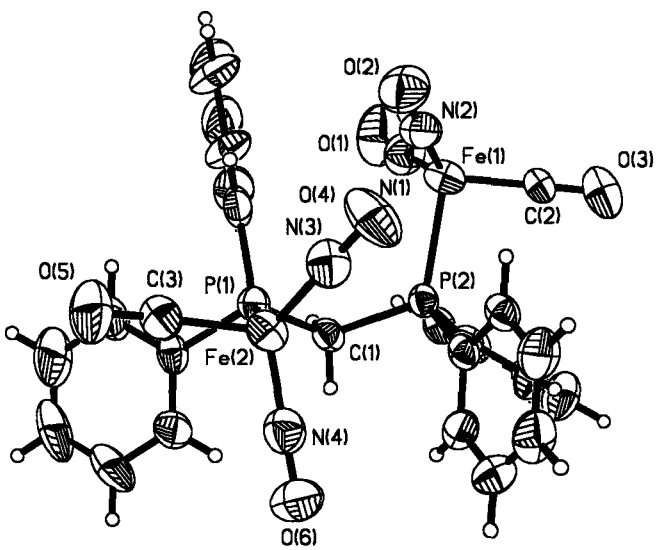


Figure 1.8. Ortep diagram of $[Fe(NO)_2(CO)]_2dppm$, shown with 50 % thermal ellipsoids.

1.5 Research Objectives

Nitric oxide's rapid reactivity with oxygen and other substances in water suggests that, in some instances, NO transport may be affected by metal ion complexation. The trend has been to detect the presence of these compounds rather than isolate them. To this day, a large number of biologically detectable EPR compounds have not been isolated. In fact, the majority of compounds made are made with P and S ligands, and a number of reviews describing these compounds are in the literature.[31,32] It has been our goal to synthesize and fully characterize a series of non-heme, non sulfur iron dinitrosyl compounds, an area of synthesis which has not previously attracted much attention. We focussed on the synthesis of biologically relevant compounds that mimic histidine iron compounds, by using a series of imidazoles (histidine is an imidazole containing amino acid), including imidazole, 1-methylimidazole, 4-methylimidazole, benzimidazole, and 5,6-dimethylbenzimidazole. These were reacted with dinitrosyldicarbonyliron to form disubstituted complexes of the form $Fe(NO)_2(L)_2$ [L = imidazole **1**, 1-methylimidazole **2**, 4-methylimidazole **3**, benzimidazole **4**, and 5,6-dimethylbenzimidazole **5**]. We emphasized characterization of **1-5** by IR, Mass spectrometry, NMR and X-ray crystallography. EPR studies are compared with previous EPR studies of biological iron dinitrosyl mimics.

2. Results and Discussion

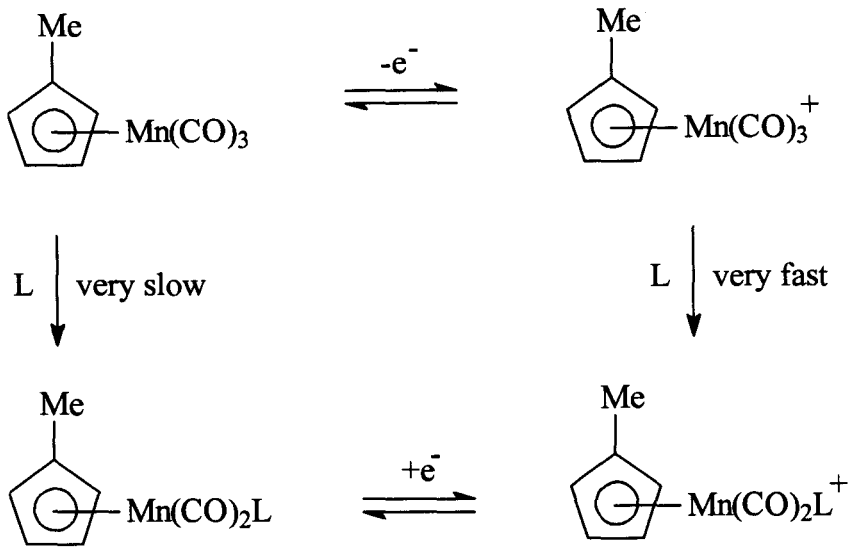
2.1 Mechanism of Reaction of iron dinitrosyl compounds with imidazole ligands.

Synthesis of the $Fe(NO)_2(L)_2$ [L = imidazole **1**, 1-methylimidazole **2**, 4-methylimidazole **3**, benzimidazole **4**, 5,6-dimethylbenzimidazole **5**] series of compounds were carried out under inert atmosphere, utilizing rigorously dried and degassed solvents. The reaction mixtures consisted of a 2:1 molar ratio of the appropriate imidazole ligand with a solution of $Fe(NO)_2(CO)_2$ dissolved in THF , ether, or dichloromethane. Upon addition of ligand, the solution turned from red to green withing two minutes, with fierce gas evolution. As well, an EPR detectable signal was observed for each reaction mixture of **1 - 5**. These observations indicate that the reaction rate is much greater than that of conventional substitution and therefore the mechanism of substitution proceeds by a pathway other than that of conventional associative substitution.

To determine the mechanism of reaction, attention must first be focussed on the formation of an EPR detectable species in each reaction mixture. The signal, centered approximately at g = 2.03G, is consistent with a 17 electron complex that has the unpaired electron situated mainly on iron. A 19 electron complex is ruled out, as these complexes typically have isotropic g-factor values < 2.000G.

A variety of 17 electron complexes have been previously studied.[33] For example, the complex $[(MeCp)Mn(CO)_3]$, while normally inert to CO substitution (it does not react

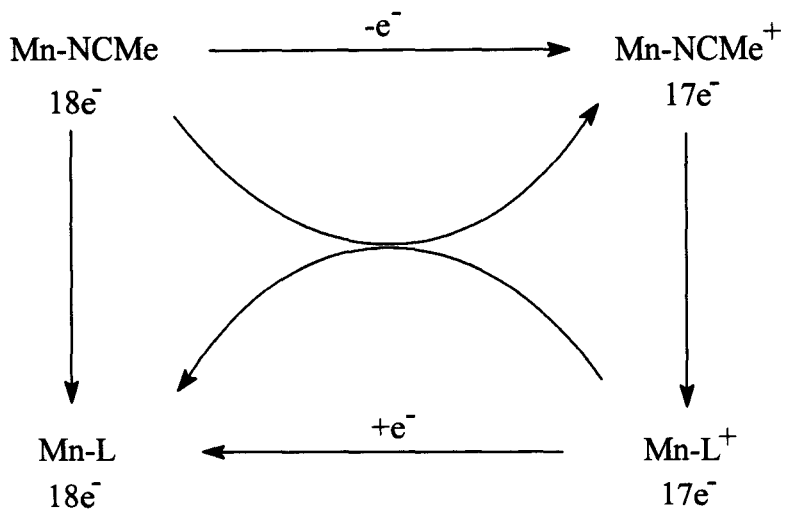
thermally with PPh_3 over 3 days at 140 °C), does undergo substitution of one or two CO



Scheme 2.1. Enhanced rate of CO substitution by oxidation of $[(MeCp)Mn(CO)_3]$ to the 17 electron $[(MeCp)Mn(CO)_3]^+$ intermediate.

ligands within milliseconds at room temperature upon oxidation in the presence of $P(OEt)_3$.[34] The chemistry involved is illustrated in Scheme 2.1. Kochi and co-workers[35,36] have established that rapid ligand substitution occurs when a slight oxidizing current is applied (or a small amount of a chemical oxidizing agent is added) to a MeCN solution of $[(MeCp)Mn(CO)_2(MeCN)]$. The electrochemical investigation showed that the reaction occurs by a "catalytic electron-transfer chain process"[35] (ETC) defined in Scheme 2.2. The catalytic cycle is initiated by oxidation of a small amount of reactant [Mn-NCMe] to yield the 17 electron $[Mn\text{-}NCMe]^+$, which rapidly substitutes PR_3 for MeCN to give $[Mn\text{-}L]^+$. It happens that the reactant [Mn-NCMe] is more easily oxidized than is the product [Mn-L], which ensures that $[Mn\text{-}NCMe]^+$ is continuously regenerated by electron transfer from [Mn-NCMe] to $[Mn\text{-}L]^+$.

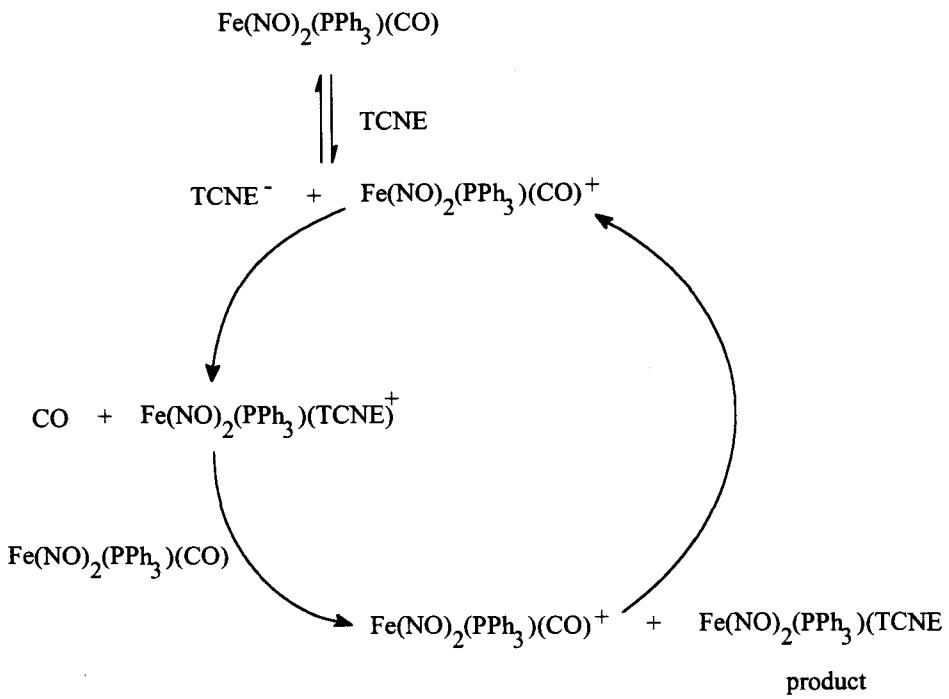
Another such reaction is that of $Fe(NO)_2(CO)(PPh_3)$ with TCNE (Scheme 2.3) as



Scheme 2.2.. Enhanced rate of CO substitution by oxidation of $[(MeCp)Mn(CO)_2(MeCN)]$ to the 17 electron $[Mn\text{-}NCMe]^+$ intermediate .

reported by Li and coworkers.[37] Generally substitution of one CO of $Fe(NO)_2(CO)_2$ usually calls for overnight stirring and replacing the second carbonyl requires heating to 85 °C for 16 h.[38] However, substitution of CO by TCNE was complete in 1-2 h.[37] The reaction was monitored by EPR and both $TCNE^-$ and $Fe(NO)_2(PPh_3)(L)^+$ radicals were observed (L may be CO or solvent). They suggested that a "radical mechanism involving a 17-electron intermediate", as shown in Scheme 3, was responsible for the enhancement of the rate of substitution without the use of an oxidizing agent such as $Co(cp)_2$, or an oxidizing potential. The TCNE ligand acts both as the oxidizing agent, and as the ligand to replace CO. Indeed, it has been shown that the reaction of $[Fe(NO)_2CO]_2dppe$ with TCNE also produces $TCNE^-$ in solution, and the mechanism proceeds *via* a 17-electron intermediate described in Scheme 2.3.

With no apparent added source of oxidizing agent, and no applied oxidizing current,



Scheme 2.3. Enhanced rate of CO substitution *via* oxidation of $Fe(NO)_2(CO)(PPh_3)$ to $Fe(NO)_2(CO)(PPh_3)^+$ by TCNE.

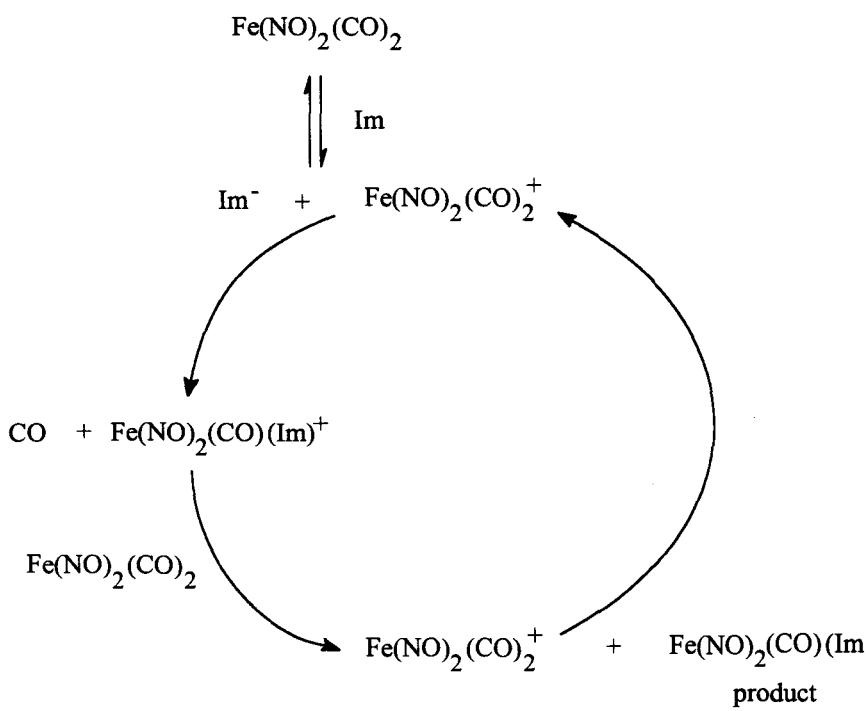
the formation of compounds **1 - 5** proceed *via* a 17 electron ETC pathway similar to that of Li. Scheme 2.4 describes the mechanistic pathway associated with the ETC substitution of CO by the series of imidazole ligands. The first run through will produce the mono-substituted $Fe(NO)_2(CO)(L)$ complex, a compound which had been detected previously[39] by IR spectroscopy during reaction of $Fe(NO)_2(CO)_2$ and 1-MeIm. A second run through of the cycle, replacing $Fe(NO)_2(CO)_2$ with $Fe(NO)_2(CO)(L)$ results in the di-substituted product. However, the proposed mechanism involves the formation of an Im^- compound, which has not been detected by EPR.

The final product was chemically sensitive to a variety of conditions. In air it

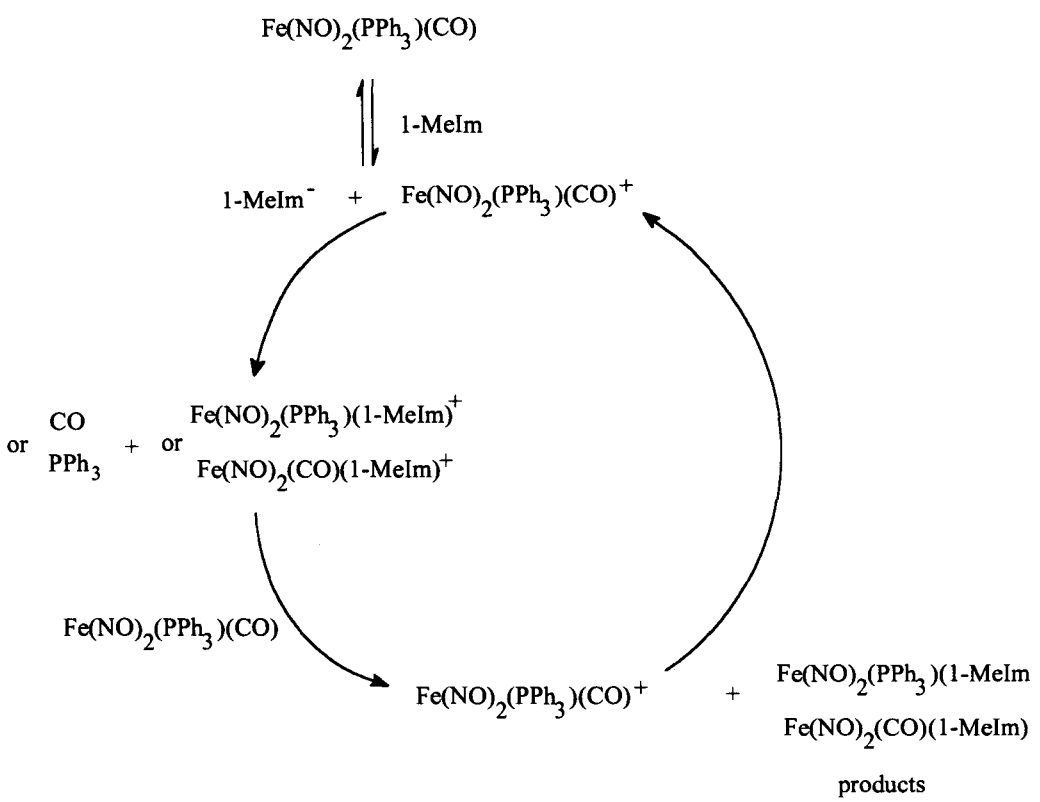
immediately turned from the characteristic green colour of the $Fe(NO)_2(L)_2$ complex to a clear brown solution, and further, to a clear solution with an orange precipitate within 7-10 minutes. Removal of solvent by reduced pressure afforded a green solid. Non-polar solvents such as ether and paraffin oil did not dissolve the product, however, the supernatant solution acquired a slight brownish tinge. The green solid did dissolve in chloroform and dichloromethane and created a clear brown solution that did not show precipitation after several days. NMR spectroscopy of deuterated chloroform solutions revealed extremely broadened lines, but nothing discernable. Methanol dissolved the green solid and retained the distinctive green colour in solution, however, this was short lived and the solution turned brown after 30 minutes. NMR spectroscopy of deuterated MeOH solutions also produced spectra with very broadened lines which could not be interpreted. The instability of these complexes may be due to the inability of the poor π-accepting ability of the imidazole ligands to stabilize the lower oxidation state of iron.[40]

In an effort to try to stabilize the final products, the compound $Fe(NO)_2(CO)(PPh_3)$ was used, with the strong π-accepting PPh_3 ligand as a stabilizer. Iron dinitrosyl products with a PR_3 ligand are relatively more stable as a solid than the starting material, $Fe(NO)_2(CO)_2$, and it was hoped that this ligand would increase the stability of a mono-substituted imidazole compound. Addition of 1-MeIm to a solution of $Fe(NO)_2(CO)(PPh_3)$

produced violent gas evolution, and a darkening of the solution from red to a very dark red/green colour, which had been observed in the formation of complexes **1-5**. Crystals were obtained which revealed $Fe(NO)_2(PPh_3)_2$ (**6**). This result was not expected, however it is easily explained using a variation of the mechanism shown in Scheme 2.4. Scheme 2.5 details the ETC pathway for formation of **6**. The first time through the cycle, both $Fe(NO)_2(PPh_3)(Im)$ and $Fe(NO)_2(CO)(Im)$ are produced. The formation of $Fe(NO)_2(CO)(Im)$ releases free PPh_3 into solution which, after a second run through the cycle, can react with $Fe(NO)_2(PPh_3)(Im)$ to give **6**.



Scheme 2.4. Mechanistic pathway for formation of the $Fe(NO)_2(L)_2$ [L = imidazole, 1-MeIm, 4-MeIm, Benzim, 5,6-dimethylbenzim] series of compounds.



Scheme 2.5. Mechanistic pathway for formation of the $Fe(NO)_2(L)_2$ [L = PPh_3] from the reaction of $Fe(NO)_2(CO)(PPh_3)$ and 1-MeIm.

2.2 Infrared Spectroscopy

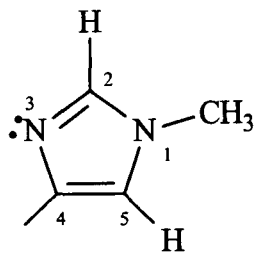
While the MNO group is expected to exhibit ν_{NO}, ν_{MN} and ν_{MNO}, only ν_{NO} has been identified in most cases in the vibrational spectra of metal nitrosyl complexes.[41] In most nitrosyl complexes, the N-O stretching frequency is observed as an intense and characteristic band in the region 1525-1940 cm^{-1}, which is associated with monodentate nitrosyl groups. Assuming the nitrosonium coordination model, the free NO^+ stretching of 2250 cm^{-1} would be expected to drop on coordination with a metal atom. This is caused by the increase in back donation of electron density from M to NO and population of the π^* orbital, which weakens the N-O bond. Conversely, a net donation of electron density from the NO group to the metal center should result in a stronger N-O bond, and hence a higher ν_{NO}. The magnitude of this decrease depends on the nature of the metal atom and the degree of σ- and π- bonding involved. This simplistic view is useful when monitoring the progress of a chemical reaction. Linear M-N-O groups absorb in the region 1650-1940 cm^{-1}, including M-N-O angles from 160 to 180°, for which the NO ligand has a formal positive charge. The stretches for the bent groups (M-N-O angle 120°) occur at lower wavenumbers (1525-1690 cm^{-1}).[42]

$Fe(NO)_2(CO)_2$ have intense stretching frequencies for both NO (1810, 1767 cm^{-1}) and CO (2087, 2038 cm^{-1}). Upon addition of the imidazole ligands, the ν_{NO}'s are lowered by approximately 140 wavenumbers and no carbonyl stretching frequencies are observed. This indicated that two Im ligands had replaced the two CO ligands. The nitrosyls fall into the region of 1650-1940cm^{-1}, indicating they are linear. Table 2.1 lists the NO stretching frequencies observed for complexes **1 - 5**.

Table 2.1 Nitrosyl stretching frequencies for compounds **1** - **5**.

Compound	ν_{NO} (cm^{-1})
1 $Fe(NO)_2(imidazole)_2$	1680, 1622
2 $Fe(NO)_2(1\text{-MeIm})_2$	1673, 1616
3 $Fe(NO)_2(4\text{-MeIm})_2$	1677, 1620
4 $Fe(NO)_2(Benzimidazole)_2$	1682, 1625
5 $Fe(NO)_2(5,6\text{-dimethylbenzim})_2$	1683, 1625

2.3 Nuclear Magnetic Resonance Spectroscopy



Numbering Scheme for 1-MeIm

The solids of the $Fe(NO)_2(L)_2$ [L = imidazole **1**, 1-methylimidazole **2**, 4-methylimidazole **3**, benzimidazole **4**, 5,6-dimethylbenzimidazole **5**] could not be purified by conventional means. The NMR spectroscopy was therefore carried out using reaction mixtures of the imidazole series of compounds in deuterated solvents, such as *d*-chloroform and *d*-methanol (the deuterated solvents were rigorously dried over CaH_2). Analysis of the spectra proved difficult, as obvious line broadening occurred from paramagnetic species in solution. Repeated attempts produced only one spectrum, that of **2**, which could be deciphered. The proton spectrum of **2**, shown in Figure 2.1, reveals a mixture of 1-MeIm and $Fe(NO)_2(1\text{-MeIm})_2$ in solution. The broad signal at 8.79ppm is attributed to H2 and H4 of **2** (see 1-MeIm diagram above for numbering scheme). It is believed that the resonances of H2 and H4 are similar, and with line broadening, only one broad signal is observed. The 1-MeIm ligand act as an electron donor, and so the protons of H2 and H4 are deshielded upon complexation with the iron and are shifted further downfield with respect to the free 1-MeIm molecule. The signal at 4.99ppm is assigned to H5, which is not subjected to any deshielding by complexation. The broad peak at 3.97 ppm is assigned to the CH_3 group. The peaks at

7.68, 7.10, 6.87, and 3.68 ppm are assigned to H2, H4, H5, and CH_3 of the free 1-MeIm ligand, respectively.

The ^{13}C spectrum, shown in Figure 2.2, also reveals a mixture of 1-MeIm and $Fe(NO)_2(1\text{-MeIm})_2$ in solution. The small signals at 226.2 and 225.6 ppm are attributed to either of the C2 and C4 carbons. Again, these atoms are affected by the deshielding which occurs upon complexation. Definitive assignment of these two atom resonances was not made. The peak at 143.4 ppm is assigned to the C5 carbon and the broad peak at 38.3 ppm is attributed to the CH_3 carbon. The resonance peaks at 143.6, 134.2, 123.1, and 34.2 ppm arise from the C2, C4, C5 and CH_3 carbons of the free 1-MeIm ligand, respectively.

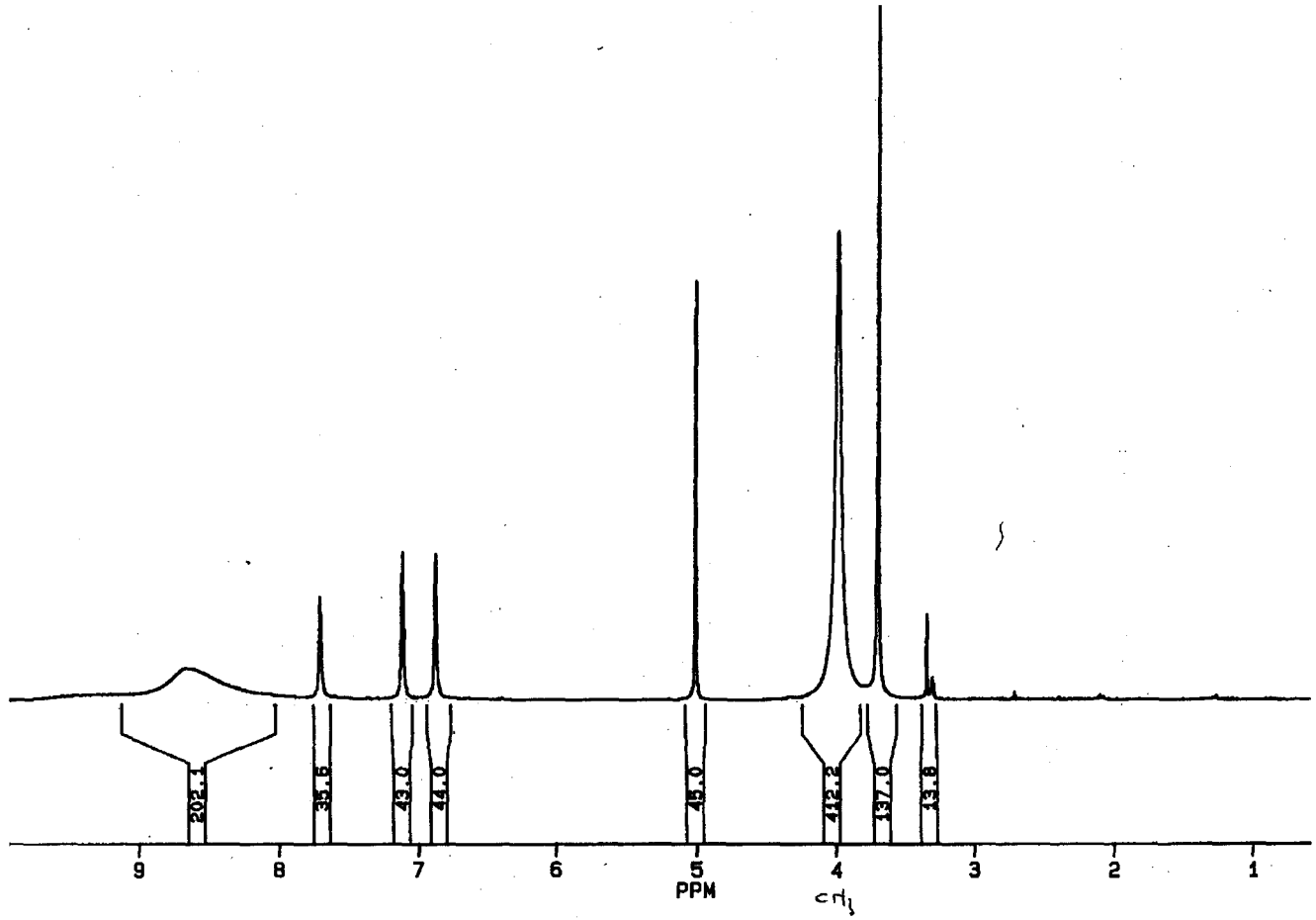


Figure 2.1. ^{1}H NMR spectrum of $Fe(NO)_2(1\text{-MeIm})_2$ in deuterated methan

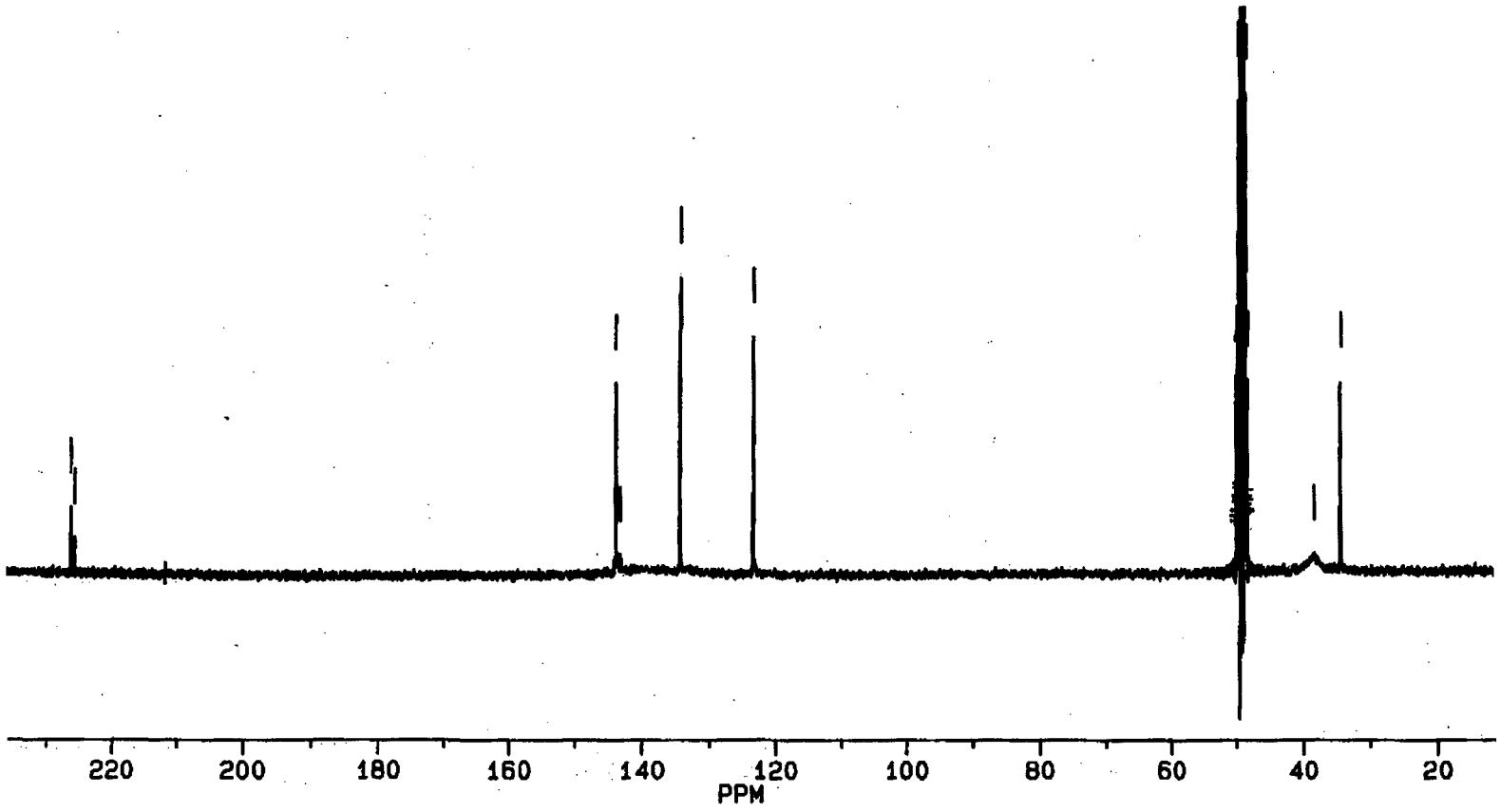


Figure 2.2. ^{13}C NMR spectrum of $Fe(NO)_2(1\text{-MeIm})_2$ in deuterated methan

2.4 EPR Spectroscopy

Electron paramagnetic resonance spectroscopy (EPR) has been one of the most commonly employed techniques for the characterization of iron dinitrosyl complexes. Although solution EPR cannot be used to determine the geometry of complexes, the spectra are useful as a means of confirming the presence of the desired product. For example, Martini and co-workers[42] reported a study on a mixture of urea and an $Fe(NO)_2$ complex. Urea (H_2N-CO-NH_2) can be expected to bind through either its carbonyl oxygen atom, or one of the two nitrogen groups. The spectrum of $Fe(NO)_2(urea)_2$ revealed a five line spectrum ($g = 2.034$, $a_n = 2.2G$) which indicated the interaction of the unpaired electron with only two equivalent nuclei of ^{14}N of the nitrosyls. The urea molecules are therefore bound to the $Fe(NO)_2^+$ group by the carbonyl oxygen. In a similar aqueous study with imidazole,[43] the spectrum obtained consisted of nine hyperfine components spaced about 2.5 G apart, and indicated a compound with two equivalent ^{14}N nuclei from the nitrosyl groups and two equivalent ^{14}N nuclei from the imidazole groups, each with the same hyperfine coupling constant.

In the course of study of $Fe(NO)_2(CO)_2$ with imidazole ligands, neutral compounds of the form $Fe(NO)_2(L)_2$ [L = imidazole **1**, 1-methylimidazole **2**, 4-methylimidazole **3**, benzimidazole **4**, 5,6-dimethylbenzimidazole **5**] were expected to be produced. However, NMR characterization proved difficult because of extensive line broadening. This suggested that a paramagnetic species was present in solution. EPR studies did reveal that a paramagnetic species was present in solution, which is believed to be a 17 electron, iron dinitrosyl intermediate involved in the formation of the 18 electron, $Fe(NO)_2(L)_2$ complex.

The g-values and hyperfine coupling constants observed for compounds **1 - 5** are listed in Table 2.2. Spectra simulation have been performed and are consistent with experimental data. Figures 2.3-2.7 show the experimental (top) and simulated (bottom) spectra for each compound.

Table 2.2. g values and hyperfine coupling constants for $Fe(NO)_2(L)_2^+$ compounds. The number in parentheses is the number of nuclei to which the coupling belongs.

Compound	g-value	a_n
$Fe(NO)_2$(imidazole)$_2$	2.0344	3.3 (1), 2.4 (1), 2.1 (2)
$Fe(NO)_2$(1-MeIm)$_2$	2.0275	2.9 (2), 2.6 (2)
$Fe(NO)_2$(4-MeIm)$_2$	2.0336	3.1 (1), 2.5 (1), 2.2 (2)
$Fe(NO)_2$(benzimidazole)$_2$	2.0341	3.8 (1), 2.4 (1), 1.9 (2)
$Fe(NO)_2$(5,6-dimethylbenzim)$_2$	2.0344	3.9 (1), 2.2 (2)

Compounds **1-5** are all centred around 2.03 G, which is typical for iron dinitrosyl radicals with an unpaired electron localized on Fe as discussed by Li and co-workers.[44] The EPR spectra of compound **1,** displayed in figure 2.3, shows a signal at 2.0343 G, that consists of 10 lines. Simulation reveals that the signal arises from the two equivalent ^{14}N nuclei of the nitrosyl ligands with a hyperfine coupling constant of 2.1 G and two inequivalent ^{14}N nuclei from the imidazole ligands with a coupling constant of 3.2 and 2.4 G. This experiment was

carried out in tetrahydrofuran, whereas previous studies by Martini[45] were carried out in aqueous solution which affects the g-value. The nine line spectrum reported was not symmetric and obviously consisted of four nuclei that were not mutually equivalent as they have suggested. Simulations were not performed by Martini confirm the coupling constants. Compound **2**, whose EPR spectrum is shown in Figure 2.4, produces a signal centred at 2.0275 G, and is comprised of nine lines. Simulation reveals two equivalent ^{14}N nuclei from the nitrosyl ligands and two equivalent 1-MeIm ligands with coupling constants of 2.6 and 2.9 G, respectively. Compound **3** (Figure 2.5) produces a 10 line spectrum centred at 2.0337 G. The spectrum contains two equivalent ^{14}N nitrosyl groups, with a coupling constant of 2.2 G, and two inequivalent 4-MeIm ligands with coupling constants of 3.1 and 2.5 G. The spectrum of compound **4**, shown in Figure 2.6, is centred at 2.0341 G and consists of eleven lines. Simulation revealed a compound with two equivalent ^{14}N nuclei from the nitrosyls, with hyperfine coupling of 1.9 G and two inequivalent ^{14}N nuclei from the BenzIm groups with hyperfine coupling equal to 3.8 and 2.4 G. The EPR spectrum of **5,** shown in Figure 2.7, was centred at 2.035 G and consisted of 9 lines. The simulation for this spectrum revealed that only three ^{14}N nuclei were producing the hyperfine interactions. Two equivalent nitrosyl groups gave rise to a coupling of 2.2 G, and only one ^{14}N nucleus produces a coupling of 3.9 G. The reaction mixture of $Fe(NO)_2(CO)_2$ and 5,6-dimethylbenzimidazole was in a 1:2 ratio to facilitate the substitution of two carbonyls by the imidazole ligands. It is unknown as to why only one 5,6-dimethylbenzimidazole ligand was involved in substitution.

Figure 2.3. EPR spectrum (above) and simulation (below) of $Fe(NO)_2(imidazole)_2$.

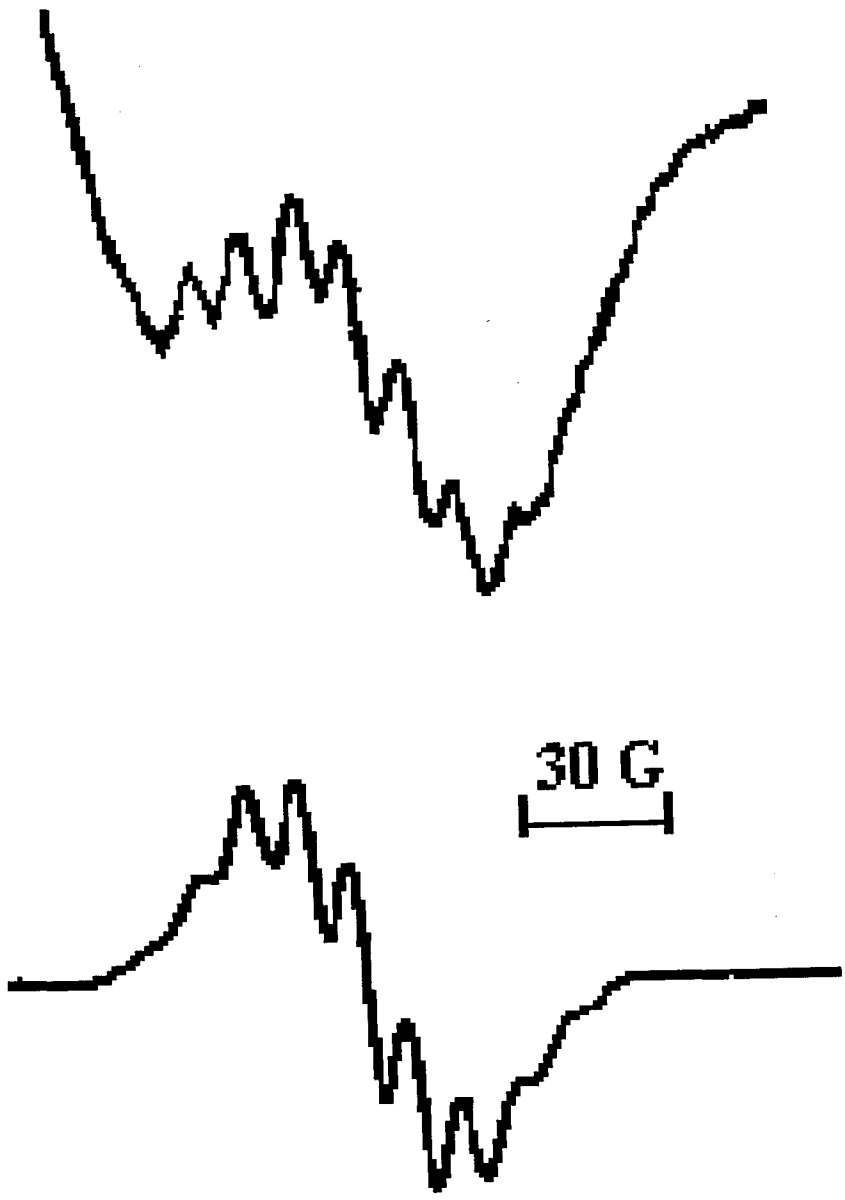


Figure 2.4. EPR spectrum (above) and simulation (below) of $Fe(NO)_2(1\text{-MeIm})_2$.

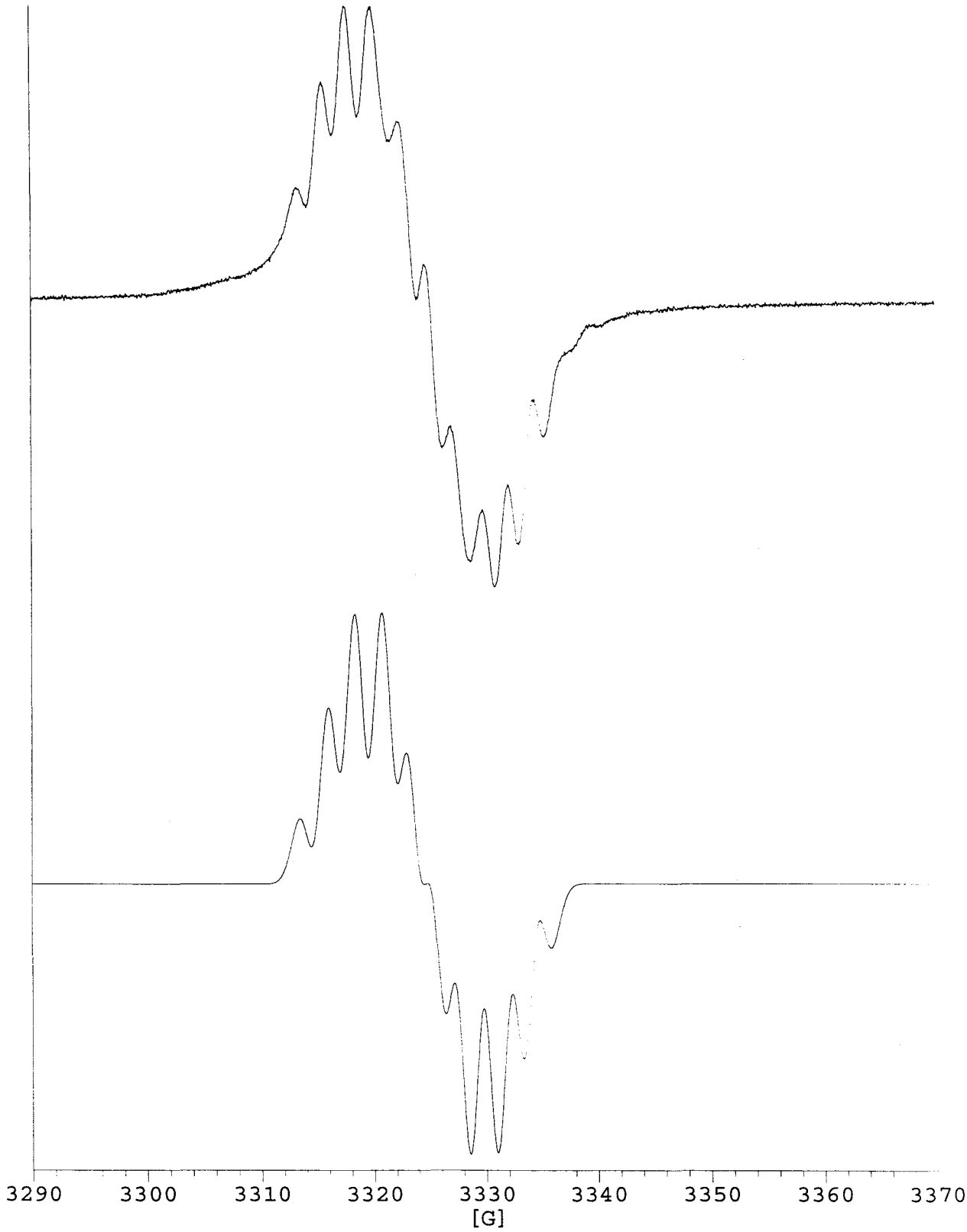


Figure 2.5. EPR spectrum (above) and simulation (below) of $Fe(NO)_2(4\text{-MeIm})_2$.

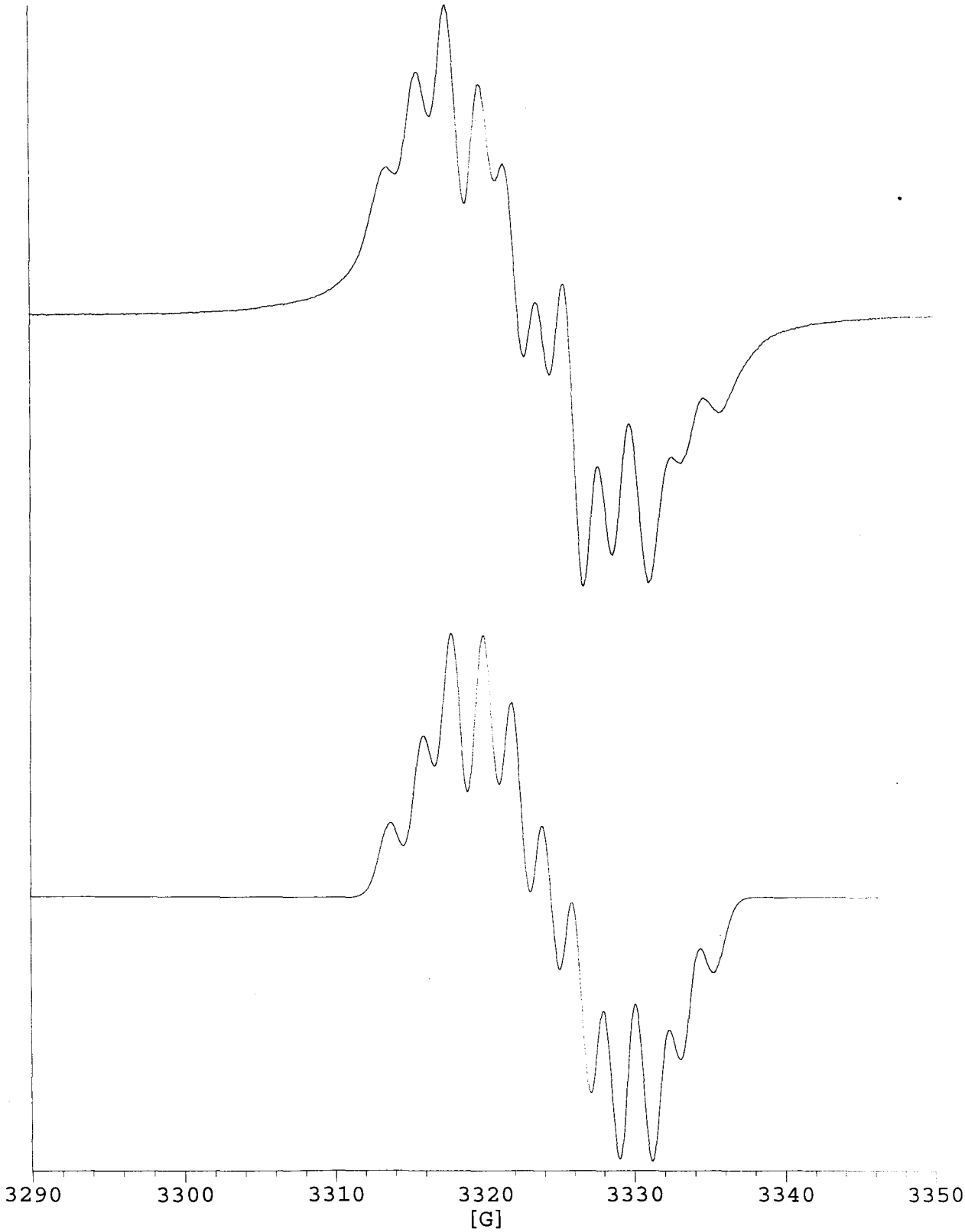


Figure 2.6. EPR spectrum (above) and simulation (below) of $Fe(NO)_2$(benzimidazole)$_2$.

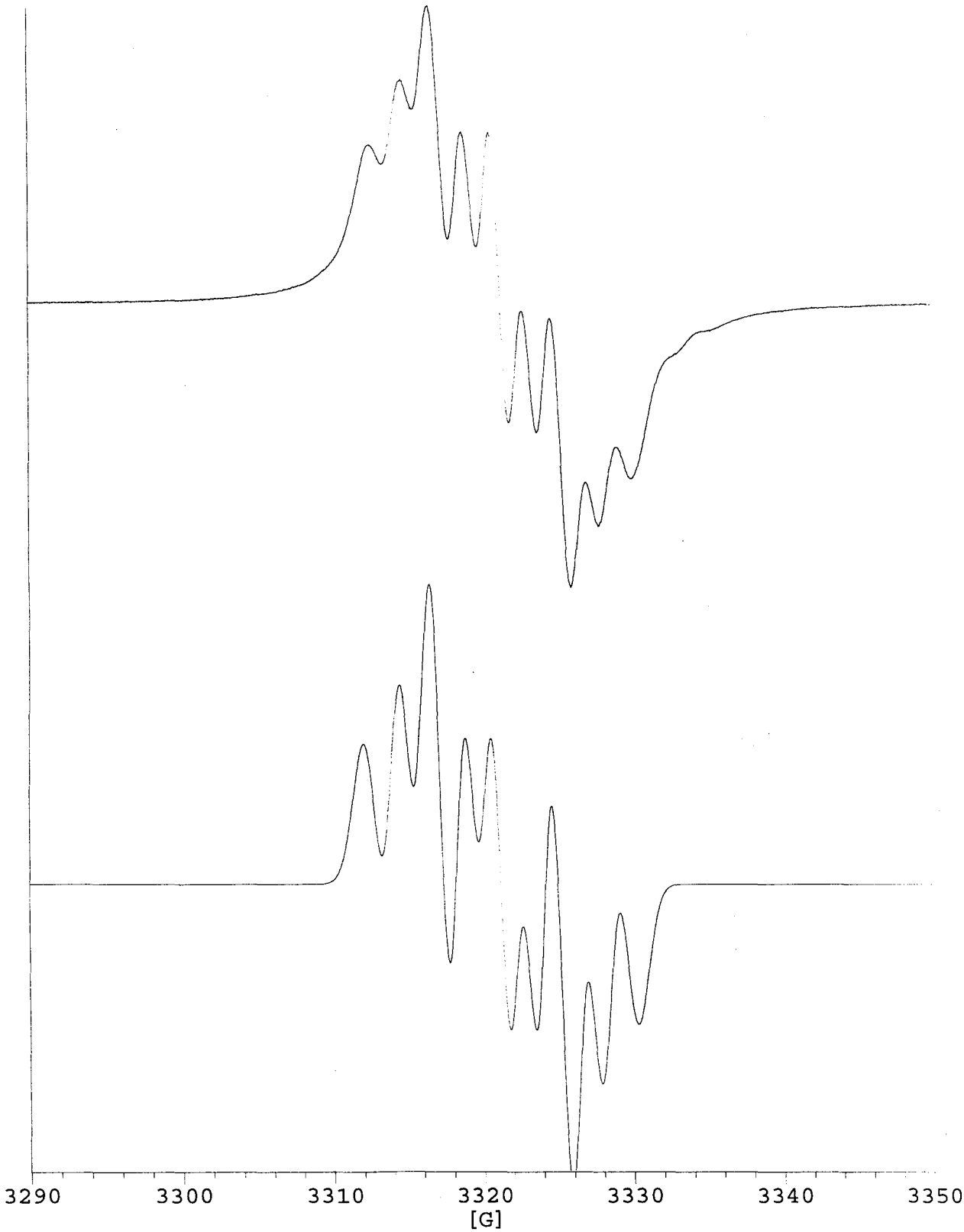


Figure 2.7. EPR spectrum (above) and simulation (below) of $Fe(NO)_2$(5,6-dimethylbenzimidazole)$_2$.

2.5 X-Ray Crystallography

Single crystals of **2** were obtained from ether solution. The crystals were placed in a petri dish containing dry paraffin oil. The oil had been dried over sodium metal and purged with nitrogen for one week prior to use. A single green crystal, 0.06 x 0.25 x 0.30mm was mounted on a glass fibre, with the paraffin oil as the adhesive. The X-ray crystal structure of **2**, $Fe(NO)_2$(1-methylimidazole)$_2$ is shown in Figure 2.8. It crystallized as a monoclinic system, with a space group of C2/c and with the following dimensions: a = 13.985(5) Å, b = 11.529 (5) Å, c = 15.471(4) Å, $\alpha = 90°$, $\beta = 91.72(2)°$, $\gamma = 90°$, V = 2493(2) $Å^3$, Z = 8.

The iron atom is situated in a *pseudo*-tetrahedral environment, with two coordinated NO groups attached through the nitrogen and two coordinated 1-methylimidazole ligands attached by the sp^2 hybridized nitrogen. The nitrosyls are linear, having angles of 167.5(3)° and 170.1(3)°. They are situated with an angle of 116.5° between N_1-Fe-N_2. The O_1-Fe-O_2 angle is 107.3°, and so forms an "attracto" conformation where O-M-O < N-M-N. This is in accord with the proposal that for complexes with N-M-N bond angles of less than 130°, the two O atoms bend towards each other.[46] The angle between N_3-Fe-N_5 is 91.20°. The nitrosyl groups are much better π-acceptors than the 1-MeIm ligands and will necessarily have a larger angle between them than the corresponding 1-MeIm ligands.[47]

Since the 1-MeIm ligand is a poorer π-acceptor than PR_3, dppe or dppm, the imidazole complex would be expected to have shorter Fe-N(O) and longer N-O bond distances than the phosphorous complexes. The π-acidity of the P ligand would compete with the π-accepting ability of N(O) and would, in effect, cancel each other out. The imidazole complex would not be able to compete with the Fe-N(O) backbonding, resulting

in a shorter Fe-N(O) and longer N-O bond. Table 2.3 compares the bond distances of some iron dinitrosyl complexes. The dppe and dppm complexes follow this trend loosely, with somewhat longer Fe-N bonds and only slightly longer N-O bonds. The PPh_3 complex does not follow this trend, with bond distances similar to that of the 1-MeIm complex.

Table 2.3. Comparison of iron dinitrosyl bond lengths (in Å).

	$Fe(NO)_2(1\text{-MeIm})_2$	$[Fe(NO)_2(CO)]_2dppe$	$[Fe(NO)_2(CO)]_2dppm$	$Fe(NO)_2(PPh_3)_2$
Fe-N (avg)	1.649	1.680	1.685	1.651
N-O (avg)	1.189	1.170	1.171	1.188

If a plane were to pass horizontally through each of the flat 1-MeIm ligands, the two planes would be skewed 106.7° from each other. The methyl groups on the N4 and N6 atoms 1-MeIm point to the same side of the molecule, bestowing close to a C_s symmetry rather than a C_2 symmetry. A crystal packing diagram, shown in Figure 2.9, reveals a layering of 1-MeIm ligands (not to be confused with π stacking), a phenomenon previously encountered in iron dinitrosyl compounds.[48] Closer inspection shows that each of two H's of a methyl group is sandwiched between two nitrosyls, the two nitrosyls coming from different molecules. Each hydrogen is in close proximity with the oxygen of the NO ligands, which may prove to be a hydrogen bonding effect and a reason why the remaining four imidazole complexes do not readily form crystals. The third hydrogen of the methyl group is not involved in hydrogen bonding.

The crystal structure of **6** has been previously reported.[49] The unit cell dimensions for both refinements match, however, the quality of the data of the previous study is questionable. Firstly, the thermal parameters were not reported. Secondly, they did not indicate the data to parameter ratio or the 2270 total reflections collected within $2\theta \leq 54°$. Only 1198 independent non-zero reflections were used in the refinement. If the total number of parameters was the same as in the refinement of **6** (total of 255 parameters), the data to parameter ratio would be less than 5:1, an unsatisfactory data set by today's standards and prone to large errors. A new definition of $Fe(NO)_2(PPh_3)_2$ is necessary and is described below.

The refinement of **6** used 3208 independent reflections for 255 parameters, or a ratio of 12.5:1. Figure 2.10 shows the ortep diagram of **6**, $Fe(NO)_2(PPh_3)_2$. The iron is situated in a *pseudo*-tetrahedral environment with two coordinated NO groups attached through the nitrogen and two triphenyl phosphine groups attached through the phosphorous atom. The nitrosyls are linear, having angles of 177.7(4)°. The O-Fe-O angle is less than the N-Fe-N angle, and fits the definition of an 'attracto' conformation. The angle of N-Fe-N is 124.5(3)°. The angle of P-Fe-P is 111.9(6)°. The nitrosyl groups are better π-acceptors than the PPh_3 ligands and therefore have the larger angle between them. In comparison with **2**, the greater π-accepting ability of the PPh_3 ligand widens the P-Fe-P angle of **6** to 111.9(6)°, whereas the lesser π-acidity of the 1-MeIm group folds in the N_3-Fe-N_5 angle to 91.2°.

The crystal packing of **6**, shown in Figure 2.11, reveals a layering of nitrosyls and a layering of the phenyl groups as observed in the crystal packing of $[Fe(NO)_2(CO)]_2$dppe and $[Fe(NO)_2(CO)]_2$dppm.[50]

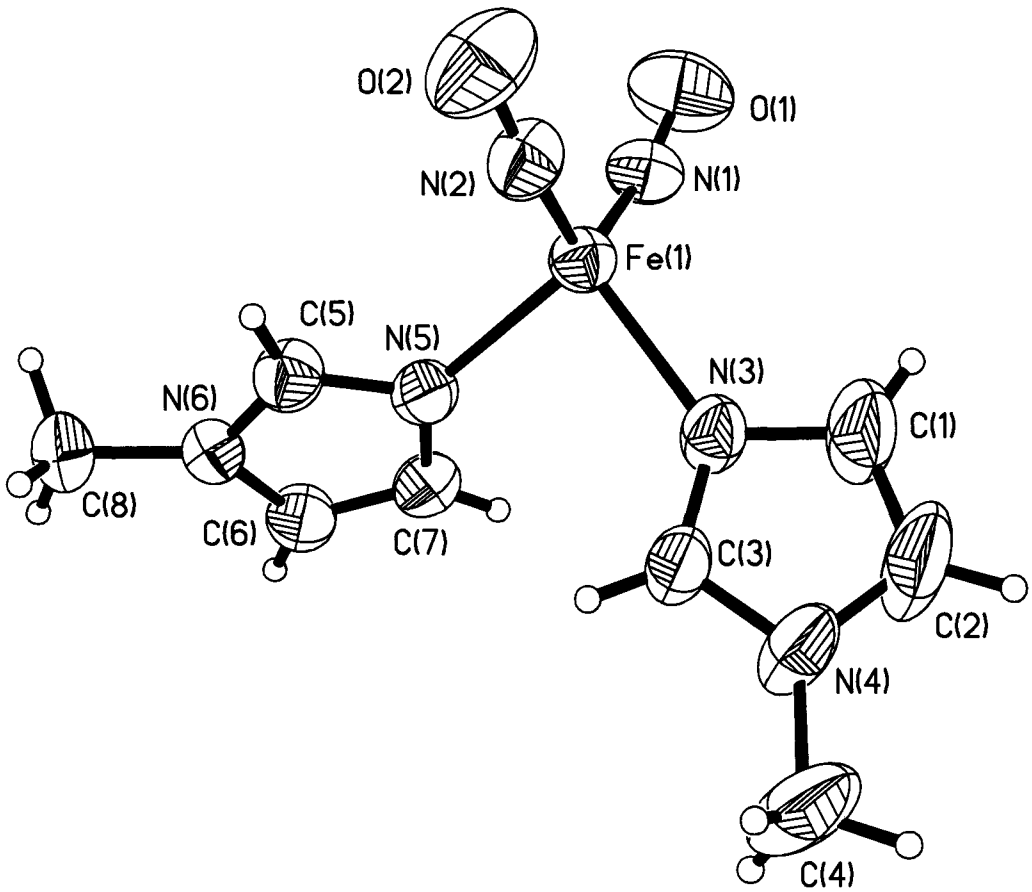


Figure 2.8. Ortep diagram of $Fe(NO)_2(1\text{-MeIm})_2$ shown at 50 % thermal ellipsoids.

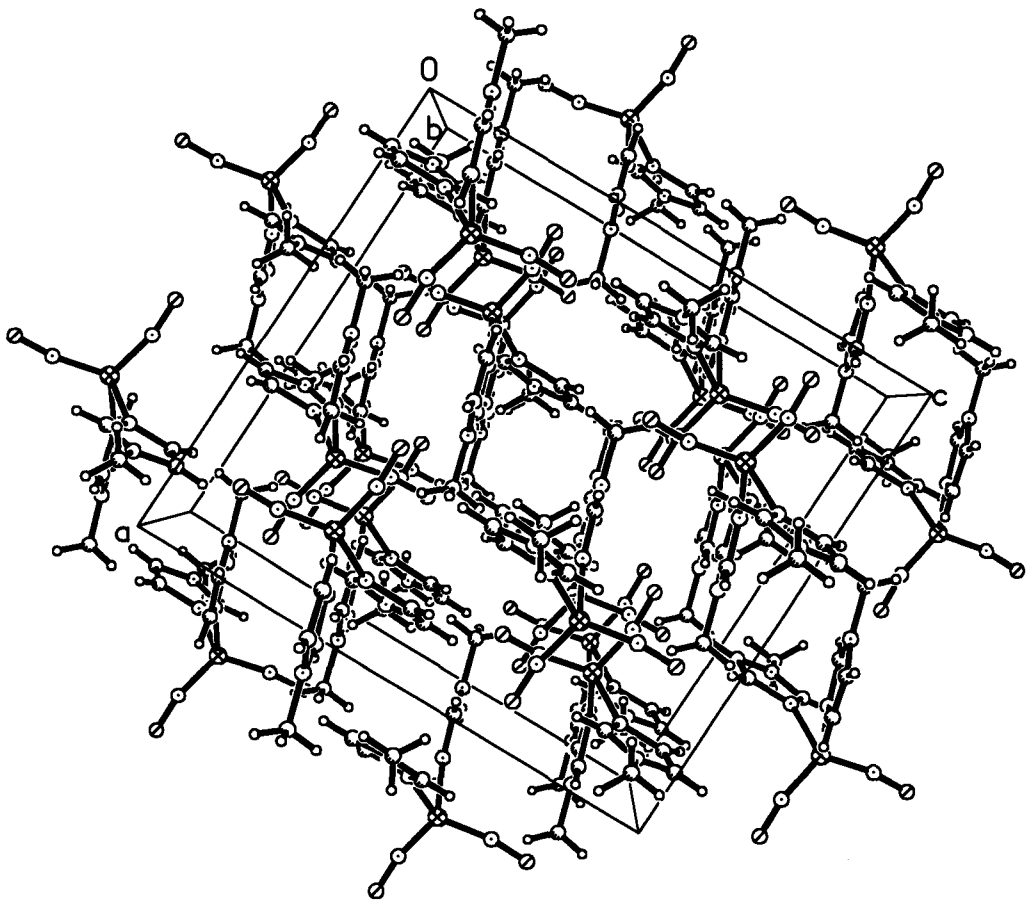


Figure 2.9. Crystal packing diagram of $Fe(NO)_2(1\text{-MeIm})_2$.

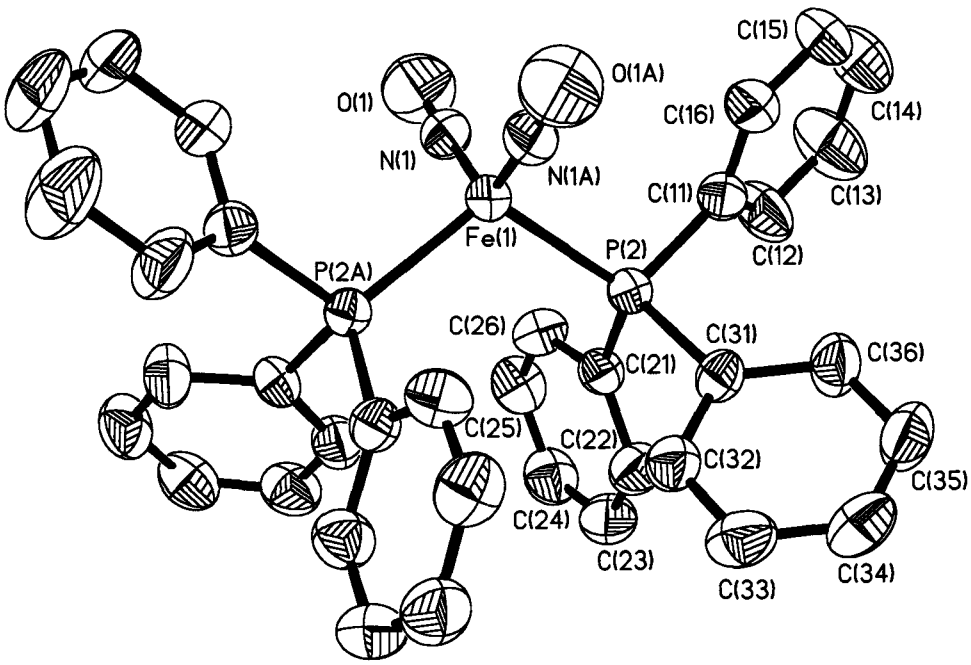


Figure 2.10. X-Ray crystal structure of **6,** shown with 50 % thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

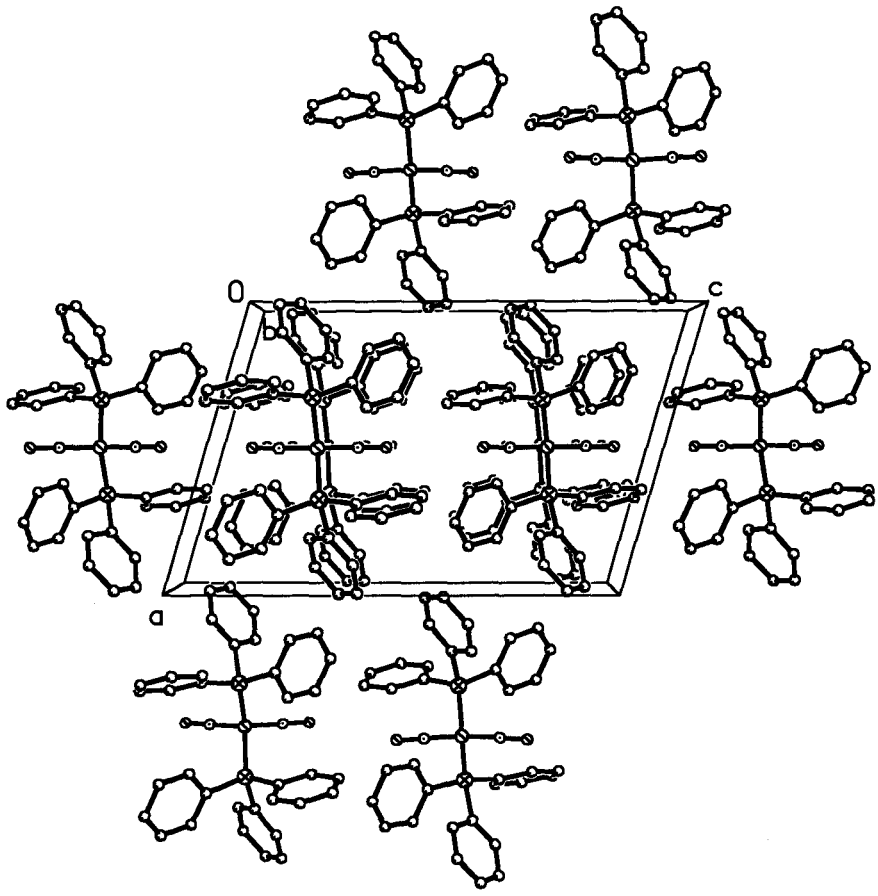


Figure 2.11. Crystal packing of **6**, viewed down the *b* axis. Hydrogen atom have been omitted for clarity.

Table 2.4. Crystal data and structure refinement for 2.

Identification code	n2
Empirical formula	C8 H12 Fe N6 O2
Formula weight	280.09
Temperature	300(2) °K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions	a = 13.985(5) Å α = 90°. b = 11.529(5) Å β = 91.72(2)°. c = 15.471(4) Å γ = 90°.
Volume, Z	2493(2) Å^3, 8
Density (calculated)	1.492 Mg/m^3
Absorption coefficient	1.210 mm^-1
F(000)	1152
Crystal size	.06 x .25 x .30 mm
Theta range for data collection	2.29 to 26.44 °.
Limiting indices	-17<=h<=17, -14<=k<=14, -13<=l<=19
Reflections collected	9872
Independent reflections	2408 [R(int) = 0.0439]
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2408 / 0 / 179
Goodness-of-fit on F^2	1.112
Final R indices [I>2sigma(I)]	R1 = 0.0419, wR2 = 0.0928
R indices (all data)	R1 = 0.0633, wR2 = 0.1034
Largest diff. peak and hole	0.330 and -0.237 e.A^-3

Table 2.5. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for 2. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Fe(1)	2025(1)	7309(1)	2075(1)	40(1)
N(1)	3140(2)	6942(3)	1892(2)	49(1)
N(2)	1799(2)	7754(2)	3062(2)	51(1)
N(3)	1083(2)	6097(2)	1588(2)	47(1)
N(4)	-259(2)	5243(3)	1185(2)	65(1)
N(5)	1505(2)	8530(2)	1227(2)	42(1)
N(6)	1202(2)	10293(2)	751(2)	42(1)
O(1)	3975(2)	6742(3)	1919(2)	82(1)
O(2)	1782(2)	8090(3)	3787(2)	87(1)
C(1)	1193(3)	4930(4)	1650(4)	83(2)
C(2)	371(4)	4402(4)	1411(4)	99(2)
C(3)	196(2)	6247(3)	1308(2)	49(1)
C(4)	-1253(3)	5084(4)	889(3)	94(2)
C(5)	1317(2)	9618(3)	1437(2)	46(1)
C(6)	1327(3)	9610(3)	44(2)	51(1)
C(7)	1502(3)	8535(3)	340(2)	48(1)
C(8)	1019(3)	11536(3)	767(2)	57(1)

Table 2.6. Bond lengths [A] and angles [deg] for 2.

Fe(1)-N(1)	1.648(3)
Fe(1)-N(2)	1.650(3)
Fe(1)-N(5)	2.044(3)
Fe(1)-N(3)	2.048(3)
N(1)-O(1)	1.189(3)
N(2)-O(2)	1.188(4)
N(3)-C(3)	1.313(4)
N(3)-C(1)	1.358(5)
N(4)-C(3)	1.332(4)
N(4)-C(2)	1.350(6)
N(4)-C(4)	1.462(5)
N(5)-C(5)	1.323(4)
N(5)-C(7)	1.372(4)
N(6)-C(5)	1.321(4)
N(6)-C(6)	1.364(4)
N(6)-C(8)	1.457(4)
C(1)-C(2)	1.343(6)
C(6)-C(7)	1.341(5)
N(1)-Fe(1)-N(2)	116.57(14)
N(1)-Fe(1)-N(5)	112.76(12)
N(2)-Fe(1)-N(5)	107.78(13)
N(1)-Fe(1)-N(3)	111.28(13)
N(2)-Fe(1)-N(3)	114.43(13)
N(5)-Fe(1)-N(3)	91.20(11)
O(1)-N(1)-Fe(1)	167.5(3)
O(2)-N(2)-Fe(1)	170.1(3)
C(3)-N(3)-C(1)	104.9(3)
C(3)-N(3)-Fe(1)	128.5(2)
C(1)-N(3)-Fe(1)	125.4(3)
C(3)-N(4)-C(2)	106.4(3)
C(3)-N(4)-C(4)	126.9(4)
C(2)-N(4)-C(4)	126.7(4)
C(5)-N(5)-C(7)	104.3(3)
C(5)-N(5)-Fe(1)	124.4(2)
C(7)-N(5)-Fe(1)	129.5(2)
C(5)-N(6)-C(6)	106.8(3)
C(5)-N(6)-C(8)	125.7(3)
C(6)-N(6)-C(8)	127.5(3)
C(2)-C(1)-N(3)	109.6(4)
C(1)-C(2)-N(4)	107.0(4)
N(3)-C(3)-N(4)	112.1(3)
N(6)-C(5)-N(5)	112.4(3)
C(7)-C(6)-N(6)	106.6(3)
C(6)-C(7)-N(5)	109.9(3)

Table 2.7. Anisotropic displacement parameters (A^2 x 10^3) for 2.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Fe(1)	39(1)	41(1)	38(1)	1(1)	1(1)	-2(1)
N(1)	41(2)	61(2)	45(2)	3(1)	-1(1)	-1(1)
N(2)	59(2)	46(2)	48(2)	-2(1)	6(1)	-6(1)
N(3)	40(2)	38(2)	63(2)	-5(1)	6(1)	2(1)
N(4)	44(2)	49(2)	101(3)	-26(2)	12(2)	-11(1)
N(5)	45(2)	42(2)	41(2)	0(1)	-2(1)	-4(1)
N(6)	43(2)	39(2)	44(2)	2(1)	-2(1)	1(1)
O(1)	44(2)	121(3)	81(2)	2(2)	2(1)	10(2)
O(2)	112(3)	93(2)	56(2)	-29(2)	20(2)	-16(2)
C(1)	61(3)	41(2)	145(5)	-10(2)	-1(3)	11(2)
C(2)	78(3)	36(2)	183(6)	-26(3)	8(3)	-2(2)
C(3)	46(2)	37(2)	64(2)	-8(2)	3(2)	-3(2)
C(4)	53(3)	94(4)	134(4)	-41(3)	1(3)	-27(2)
C(5)	54(2)	46(2)	39(2)	-1(2)	4(2)	-1(2)
C(6)	60(2)	51(2)	40(2)	2(2)	-3(2)	1(2)
C(7)	54(2)	47(2)	44(2)	-9(2)	-3(2)	-1(2)
C(8)	66(2)	40(2)	65(2)	1(2)	-2(2)	7(2)

Table 2.8. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for 2.

	x	y	z	U(eq)
H(4A)	-1396(3)	4270(4)	856(3)	141
H(4B)	-1346(3)	5427(4)	327(3)	141
H(4C)	-1670(3)	5449(4)	1288(3)	141
H(8A)	964(3)	11824(3)	186(2)	86
H(8B)	1538(3)	11922(3)	1069(2)	86
H(8C)	434(3)	11682(3)	1058(2)	86
H(1)	1742(34)	4579(46)	1771(30)	105(17)
H(2)	227(34)	3634(47)	1427(31)	108(17)
H(3)	-87(21)	6921(29)	1214(19)	39(9)
H(5)	1274(23)	9863(27)	1976(21)	41(9)
H(6)	1309(28)	9881(33)	-521(26)	73(12)
H(7)	1614(24)	7931(31)	46(22)	50(10)

Table 2.9. Crystal data and structure refinement for 6.

Empirical formula	C36 H30 Fe N2 O2 P2
Formula weight	640.41
Temperature	300(2) K
Wavelength	0.71073 A
Crystal system	Monoclinic
Space group	P2/c
Unit cell dimensions	a = 11.7076(9) Å α = 90°. b = 8.1783(5) Å, β = 106.5720(10)°. c = 17.2489(13) Å γ = 90°.
Volume, Z	1583.0(2) Å^3, 2
Density (calculated)	1.344 Mg/m^3
Absorption coefficient	0.612 mm^-1
F(000)	664
Crystal size	.08 x .10 x .12 mm
Theta range for data collection	1.81 to 26.39°.
Limiting indices	-14<=h<=14, -8<=k<=10, -21<=l<=21
Reflections collected	12269
Independent reflections	3208 [R(int) = 0.0947]
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3208 / 0 / 255
Goodness-of-fit on F^2	1.089
Final R indices [I>2sigma(I)]	R1 = 0.0652, wR2 = 0.1049
R indices (all data)	R1 = 0.1310, wR2 = 0.1304
Largest diff. peak and hole	0.257 and -0.303 e.A^-3

Table 2.10. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for 6. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Fe(1)	5000	2938(1)	7500	38(1)
N(1)	5017(3)	1999(5)	6656(3)	53(1)
O(1)	5008(4)	1279(5)	6056(3)	95(1)
P(2)	3330(1)	4489(1)	7111(1)	37(1)
C(11)	2049(4)	3144(5)	6705(3)	44(1)
C(12)	1150(4)	3494(7)	6020(4)	67(2)
C(13)	185(6)	2454(9)	5754(4)	92(2)
C(14)	105(6)	1074(9)	6154(5)	88(2)
C(15)	992(5)	692(7)	6849(4)	72(2)
C(16)	1966(4)	1717(6)	7119(3)	55(1)
C(21)	3207(3)	5938(5)	6287(3)	39(1)
C(22)	2862(4)	7545(6)	6308(3)	53(1)
C(23)	2829(5)	8585(7)	5668(4)	61(1)
C(24)	3138(4)	8051(7)	5015(4)	61(1)
C(25)	3465(5)	6452(7)	4974(3)	58(1)
C(26)	3519(4)	5414(6)	5613(3)	51(1)
C(31)	2865(3)	5677(5)	7865(2)	38(1)
C(32)	3663(4)	6792(5)	8343(3)	50(1)
C(33)	3363(5)	7708(6)	8922(3)	59(1)
C(34)	2262(5)	7537(6)	9042(3)	61(1)
C(35)	1455(5)	6470(7)	8578(3)	64(2)
C(36)	1753(4)	5544(6)	7994(3)	54(1)

Table 2.11. Bond lengths [Å] and angles [°] for 6.

Fe(1)-N(1)	1.651(4)
Fe(1)-N(1)#1	1.651(4)
Fe(1)-P(2)#1	2.2655(11)
Fe(1)-P(2)	2.2655(11)
N(1)-O(1)	1.188(5)
P(2)-C(21)	1.824(4)
P(2)-C(31)	1.827(4)
P(2)-C(11)	1.831(4)
C(11)-C(12)	1.370(7)
C(11)-C(16)	1.386(6)
C(12)-C(13)	1.384(7)
C(13)-C(14)	1.341(9)
C(14)-C(15)	1.380(9)
C(15)-C(16)	1.384(7)
C(21)-C(22)	1.378(6)
C(21)-C(26)	1.382(6)
C(22)-C(23)	1.386(7)
C(23)-C(24)	1.350(7)
C(24)-C(25)	1.370(7)
C(25)-C(26)	1.379(7)
C(31)-C(36)	1.386(6)
C(31)-C(32)	1.394(6)
C(32)-C(33)	1.373(6)
C(33)-C(34)	1.370(7)
C(34)-C(35)	1.365(7)
C(35)-C(36)	1.382(7)
N(1)-Fe(1)-N(1)#1	124.5(3)
N(1)-Fe(1)-P(2)#1	107.17(12)
N(1)#1-Fe(1)-P(2)#1	103.06(13)
N(1)-Fe(1)-P(2)	103.06(13)
N(1)#1-Fe(1)-P(2)	107.17(12)
P(2)#1-Fe(1)-P(2)	111.89(6)
O(1)-N(1)-Fe(1)	177.7(4)
C(21)-P(2)-C(31)	103.6(2)
C(21)-P(2)-C(11)	102.6(2)
C(31)-P(2)-C(11)	102.3(2)
C(21)-P(2)-Fe(1)	117.67(14)
C(31)-P(2)-Fe(1)	119.63(13)
C(11)-P(2)-Fe(1)	108.70(14)
C(12)-C(11)-C(16)	118.1(4)
C(12)-C(11)-P(2)	123.2(4)
C(16)-C(11)-P(2)	118.6(4)
C(11)-C(12)-C(13)	120.7(6)
C(14)-C(13)-C(12)	121.2(6)
C(13)-C(14)-C(15)	119.5(6)

C(14)-C(15)-C(16)	119.9(6)
C(15)-C(16)-C(11)	120.6(5)
C(22)-C(21)-C(26)	117.8(4)
C(22)-C(21)-P(2)	123.9(4)
C(26)-C(21)-P(2)	118.2(3)
C(21)-C(22)-C(23)	120.4(5)
C(24)-C(23)-C(22)	120.9(5)
C(23)-C(24)-C(25)	119.8(5)
C(24)-C(25)-C(26)	119.7(5)
C(25)-C(26)-C(21)	121.3(5)
C(36)-C(31)-C(32)	117.3(4)
C(36)-C(31)-P(2)	123.8(3)
C(32)-C(31)-P(2)	118.8(3)
C(33)-C(32)-C(31)	121.3(5)
C(34)-C(33)-C(32)	120.1(5)
C(35)-C(34)-C(33)	120.0(5)
C(34)-C(35)-C(36)	120.1(5)
C(35)-C(36)-C(31)	121.2(5)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,y,-z+3/2

Table 2.12. Anisotropic displacement parameters (A^2 x 10^3) for 6.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Fe(1)	33(1)	33(1)	50(1)	0	14(1)	0
N(1)	49(2)	45(2)	71(3)	-14(2)	28(2)	-3(2)
O(1)	113(3)	89(3)	97(3)	-45(3)	53(3)	-15(2)
P(2)	32(1)	36(1)	42(1)	-2(1)	10(1)	-1(1)
C(11)	41(2)	40(3)	51(3)	-10(2)	14(2)	-4(2)
C(12)	47(3)	69(4)	76(4)	2(3)	4(3)	-22(3)
C(13)	65(4)	105(6)	87(5)	3(4)	-11(4)	-36(4)
C(14)	57(4)	85(5)	116(6)	-19(4)	14(4)	-36(3)
C(15)	61(4)	54(4)	108(5)	-6(4)	37(4)	-19(3)
C(16)	47(3)	47(3)	71(4)	0(3)	17(3)	-4(2)
C(21)	33(2)	39(2)	42(3)	-3(2)	6(2)	-4(2)
C(22)	58(3)	50(3)	53(3)	-1(3)	20(3)	5(2)
C(23)	67(3)	45(3)	74(4)	13(3)	23(3)	6(3)
C(24)	61(3)	62(4)	60(4)	18(3)	18(3)	0(3)
C(25)	61(3)	68(4)	44(3)	5(3)	15(3)	-5(3)
C(26)	58(3)	44(3)	53(3)	-3(3)	16(2)	4(2)
C(31)	33(2)	42(2)	37(2)	0(2)	7(2)	7(2)
C(32)	41(3)	48(3)	58(3)	-8(2)	11(2)	1(2)
C(33)	60(3)	48(3)	61(3)	-13(3)	6(3)	4(3)
C(34)	69(4)	61(4)	53(3)	-14(3)	17(3)	15(3)
C(35)	55(3)	73(4)	72(4)	-15(3)	32(3)	6(3)
C(36)	37(3)	65(3)	61(3)	-17(3)	15(3)	-4(2)

Table 2.13. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for 6.

	x	y	z	U(eq)
H(12)	1227(39)	4441(54)	5731(27)	59(15)
H(13)	-334(62)	2709(80)	5249(41)	133(28)
H(14)	-609(49)	405(65)	5991(33)	94(18)
H(15)	957(42)	-260(60)	7159(29)	72(16)
H(16)	2562(37)	1363(50)	7579(26)	52(14)
H(22)	2693(31)	7917(44)	6739(23)	30(11)
H(23)	2643(39)	9670(56)	5719(27)	58(14)
H(24)	3069(40)	8695(59)	4543(31)	75(16)
H(25)	3733(40)	6081(53)	4554(29)	61(15)
H(26)	3700(35)	4351(50)	5547(24)	45(12)
H(32)	4448(39)	6843(52)	8254(25)	58(13)
H(33)	3922(41)	8456(57)	9200(28)	68(16)
H(34)	2039(38)	8036(55)	9458(27)	63(15)
H(35)	676(52)	6325(67)	8674(34)	108(21)
H(36)	1171(38)	4898(50)	7663(26)	52(13)

2.6 Mass Spectrometry

Analysis of thermally labile organometallic compounds by traditional ionization methods such as electron impact (EI) and chemical ionization (CI) is difficult. Fortunately, the problem has been alleviated to some extent by fast atom bombardment (FAB). For the series of iron dinitrosyl imidazole compounds, $Fe(NO)_2(L)_2$ [L = imidazole **1**, 1-methylimidazole **2**, 4-methylimidazole **3**, benzimidazole **4**, 5,6-dimethylbenzimidazole **5**], these conventional ionization techniques provide spectra with no observance of M+, M+ being defined as the sought after molecular ion for the four coordinate compounds of **1** - **5**. Recently, techniques have been demonstrated that combine electrospray and electrochemical

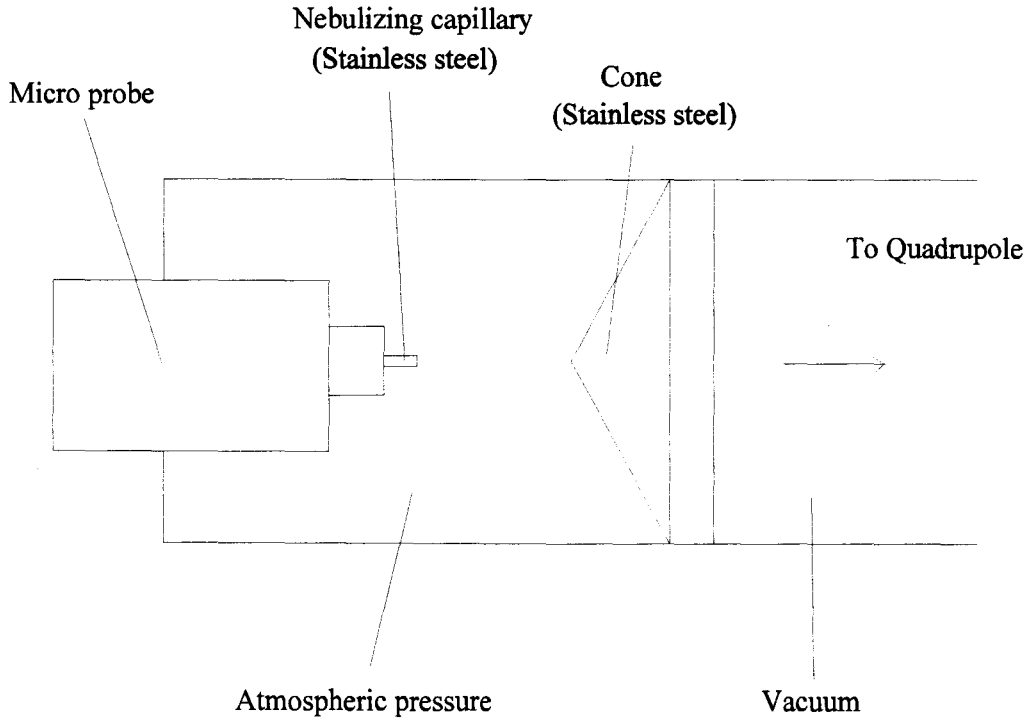


Figure 2.12. Schematic diagram of mass spectrometer ionization apparatus.

oxidation (ESCI) that produce intact molecular ions (M+) for a variety of organometallic (and organic) compounds.[51] A drawback of this procedure is the complexity of the methodology used to generate the ions, i.e. interfacing an electrochemical cell with the sample introduction system or the use of mobile phase additives such as dichlorodicyanobenzoquinone (DDQ) to promote the oxidation. Smith has recently developed a modification to the ESCI method without the use of an external electrochemical cell or addition of chemical oxidants.[52] Figure 2.12 shows a schematic diagram of the ESCI apparatus used, in which a potential difference is created between the nebulizing capillary tube (4 - 4.5 kV) and the cone (5 - 15 V). A solution containing the compound approaches the capillary tip where the compound is oxidized during a positive ion mode, under atmospheric pressure. It is believed that the ionization occurs at the tip of the nebulizing capillary when the compounds come in contact with the capillary walls.[53] The ionized compounds pass through the cone and are subjected to a vacuum as they flow towards the quadrupole detector. The mass spectroscopy experiments were carried out using reaction mixtures of the imidazole series of compounds that were worked up in a mixture of 90:10 dichloromethane/methanol, the same solvent composition as the carrier mobile phase. The M+ parent ions observed for compounds **1-5** are listed in Table 2.14. The mass spectra obtained for **1** - **5** are shown in Figures 2.13-2.17, respectively. Figures 2.18a and 2.18b show the simulated and experimental isotopic distribution of the M+ 280 peak for $Fe(NO)_2(1\text{-MeIm})_2^+$, respectively. This distribution was used to determine the iron containing compounds in the spectra.

There are two recurring, interesting aspects in each spectra besides the (M+) peaks:

1) a non iron compound that corresponds to twice the MW of the imidazole ligand plus hydrogen [2 Im + H]; and 2) repeating, higher molecular mass peaks beyond M+. The first interesting observation is a dimer of the imidazole ligand linked through a hydrogen atom. Table 2.15 lists the imidazole dimers

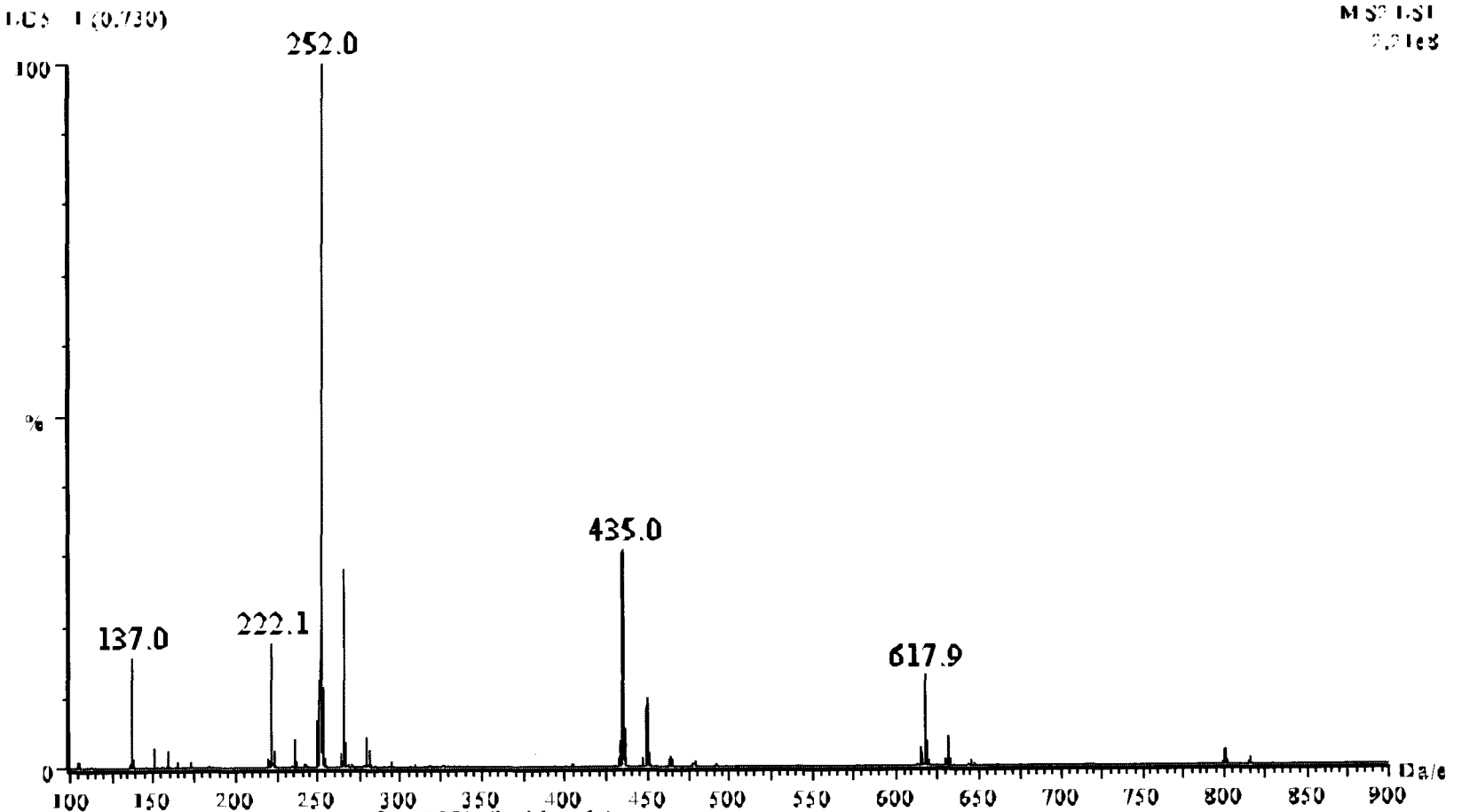


Figure 2.13. Mass spectrum of $Fe(NO)_2(imidazole)_2$

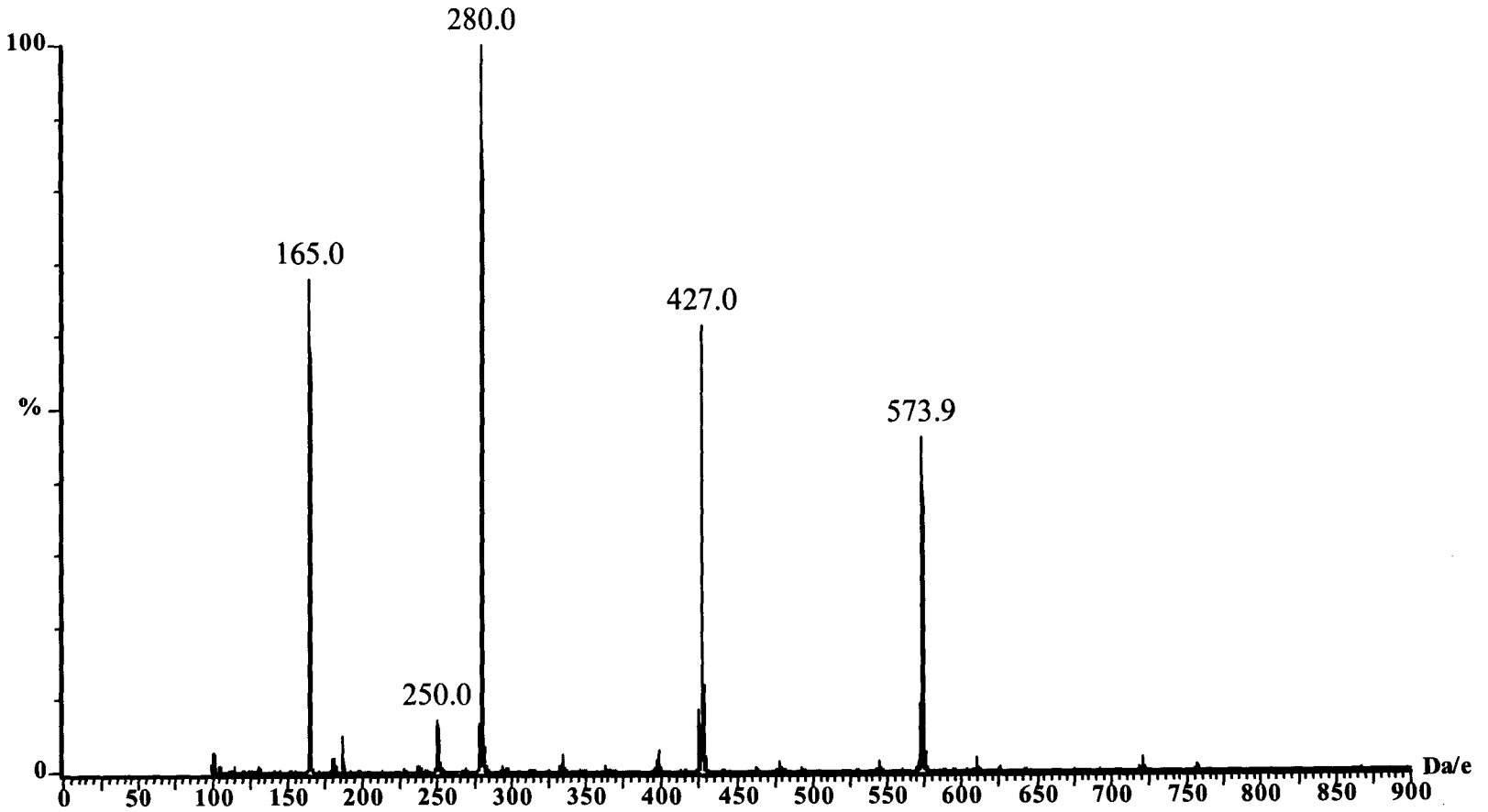


Figure 2.14. Mass spectrum of $Fe(NO)_2(1\text{-MeIm})_2$

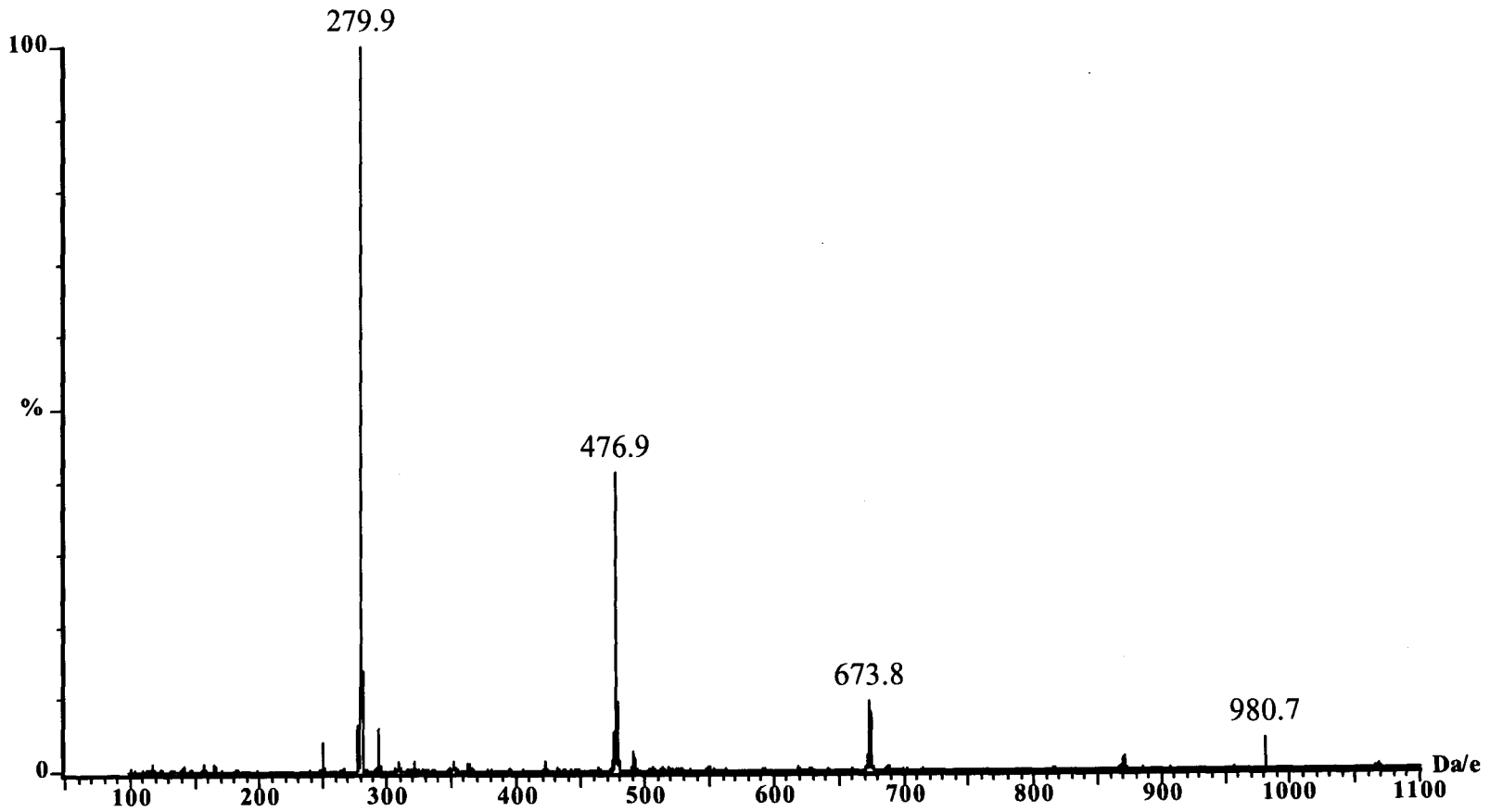


Figure 2.15. Mass spectrum of $Fe(NO)_2(4\text{-MeIm})_2$

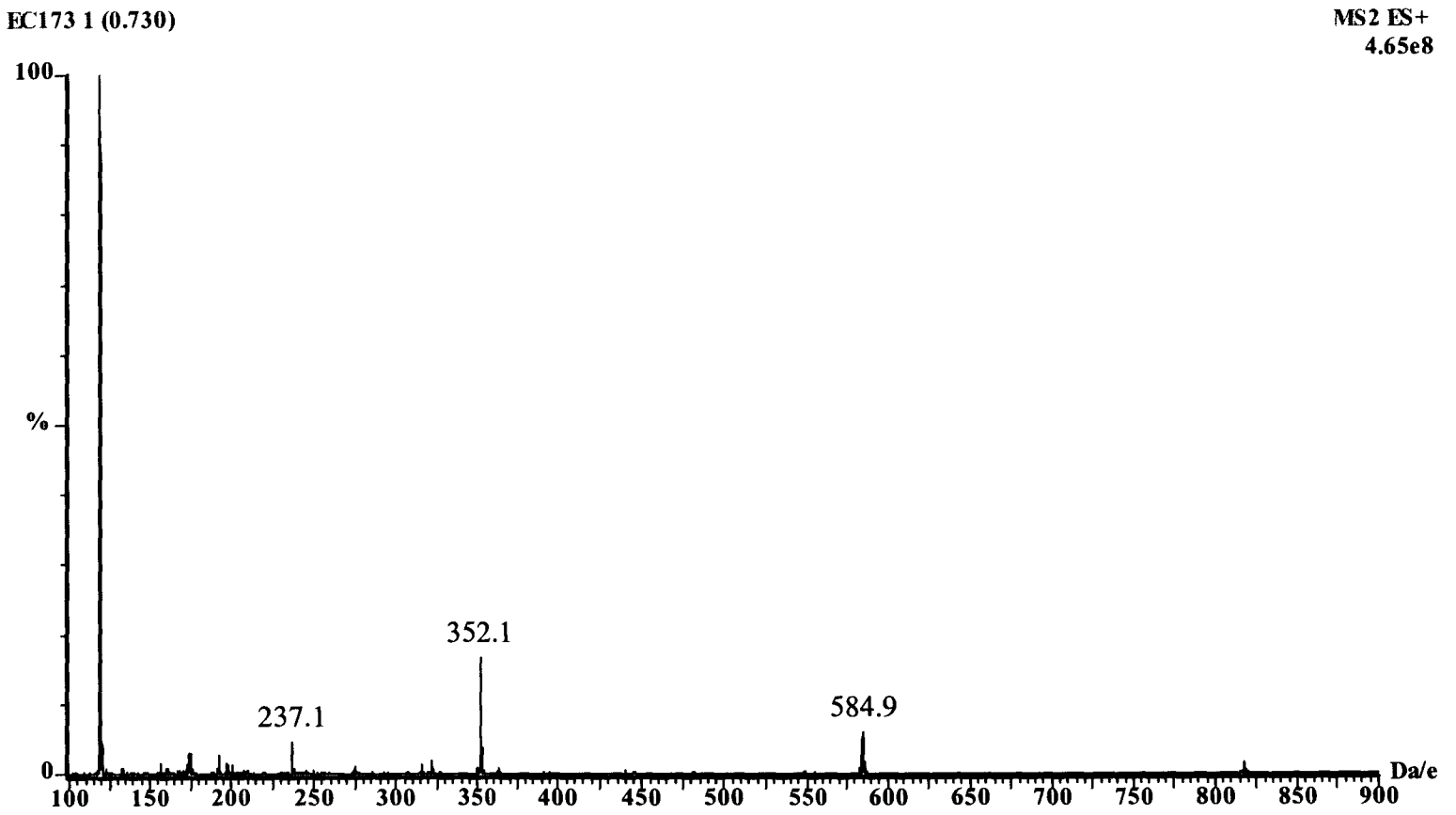


Figure 2.16. Mass spectrum of $Fe(NO)_2$(benzimidazole)$_2$

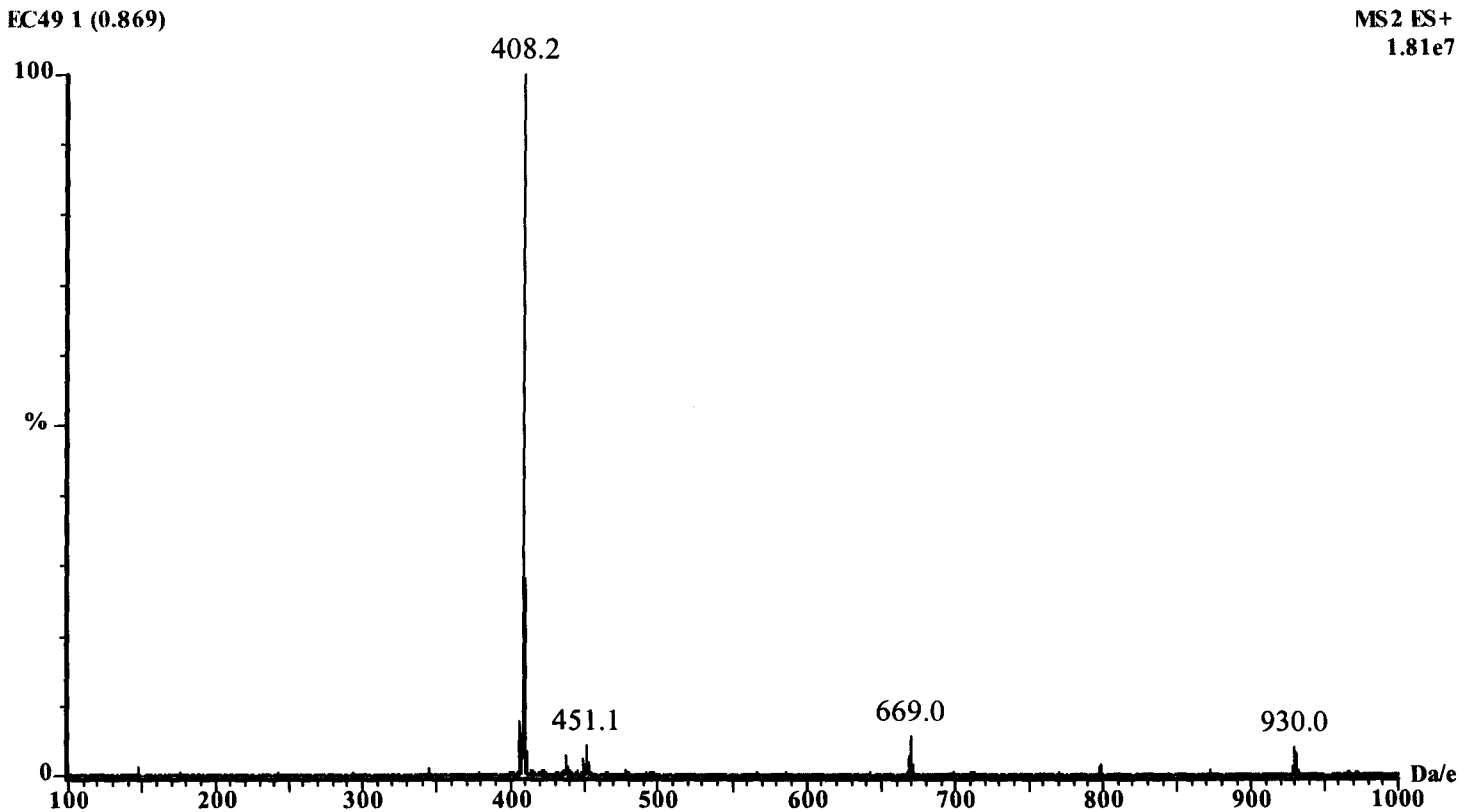


Figure 2.17. Mass spectrum of $Fe(NO)_2$(5,6-dimethylbenzimidazole)$_2$

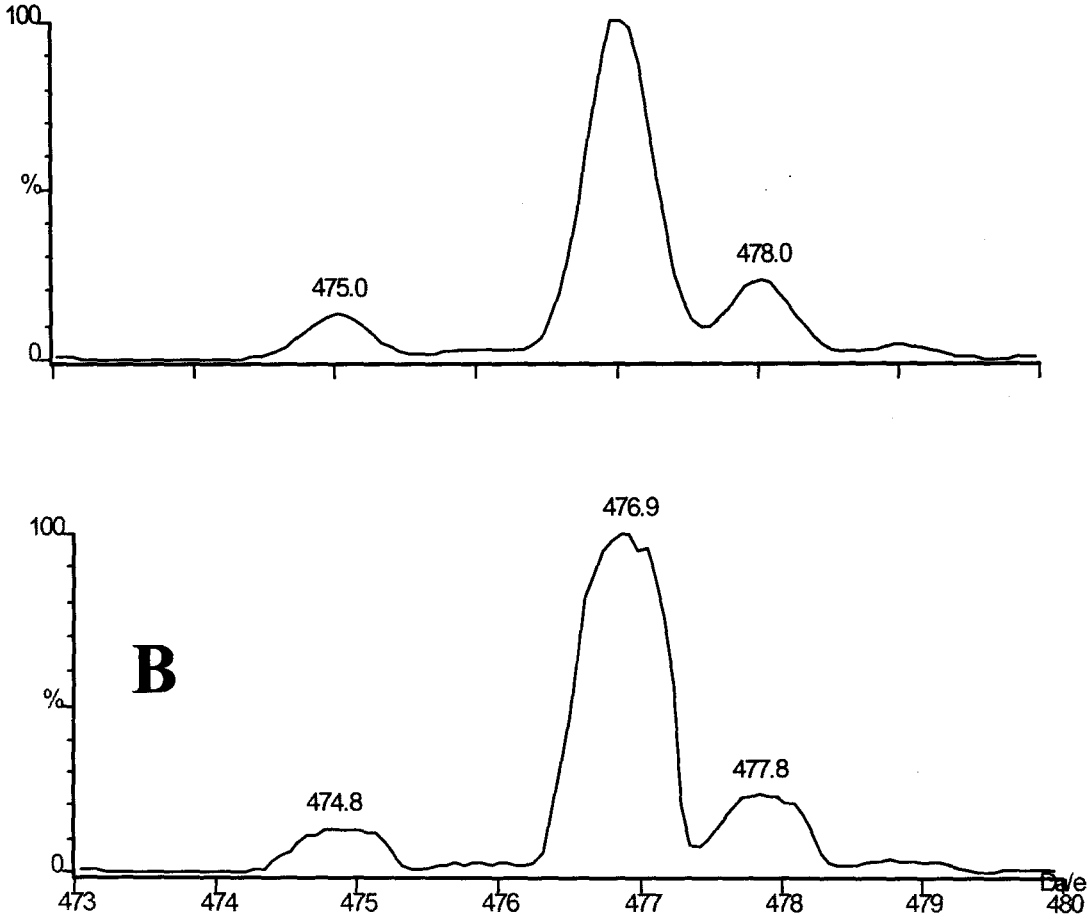


Figure 2.18. Isotopic Ratio of $Fe(NO)_2(1\text{-MeIm})_2$

found in each spectrum and Scheme 2.6 shows the proposed structures of each dimer formed. The association of imidazole ligands into long chain oligomers has been previously noted[54] and has been deemed responsible for the high melting points of imidazole, 4-MeIm, Benzim, and 5,6-dimethylbenzim (m.p. 90, 66, 170, and 204°C, respectively) relative to N-protected imidazoles (1-MeIm m.p. -6 °C).

The second unforseen feature of each mass spectrum is the appearance of higher weight molecular peaks than the parent ions. Table 2.16 lists the MW peaks greater than M+ observed for each spectrum, and the corresponding repeating mass difference between higher MW values. Each of the peaks beyond M+ is related to the M+ by the addition of a repeating mass unit, or monomer. In other words, each higher mass peak is an oligomer based on the starting M+ peak in each mass spectrum. The repeat mass unit consists of one iron, two nitrosyls, and one deprotonated imidazole ligand. For the case of $Fe(NO)_2(imidazole)_2$, the M+ peak occurs at m/z 252, with accompanying peaks at m/z 435, 618, and 801. The MW 435 peak would then consist of the M+ parent molecule, plus the iron fragment shown in Scheme 2.7. Correspondingly, the peaks at m/z 618 and 801 are larger oligomers consisting of 3 and 4 iron repeat units attached to M+. The concentration of even higher MW species are of very low intensity, and are lost in the baseline noise.

It is believed that these compounds are a direct result of the environmental conditions set by the mass spectrometer.[55] Point in proof, an experiment was carried out involving a series of injections of a reaction mixture of $Fe(NO)_2(CO)_2$ with 4-MeIm that was allowed to sit for approximately 10 minutes, 1 hour and one day. All three spectra

obtained were identical. If a polymeric species were formed in solution, a higher molecular weight distribution of ions would be expected after longer periods of time with exposure to the monomer.

Inorganic polymer species with imidazoles and Cu, Co, and Zn have been reported.[56,57,58,59] The iron compound in Figure 2.19, $[Fe_3(imid)_6(imidH)_2]_x$,[60] consists of chains of tetrahedral iron centers cross-linked *via* octahedral iron ions to generate a 3-D array. All of the iron centers are bridged to four other metal centers *via* imidazolate ions, the two remaining (trans) coordination positions of the octahedral centers being occupied by neutral imidazole molecules. The $[Fe(NO)_2(Im)_2]_x$ oligomer is a linear chain. The nitrosyl ligands replace two coordination sites available on iron and prevent the formation of cross linking between the linear chains of Fe-Im-Fe.

The fact that **2** has a repeat unit of mass 147, as shown in Figure 2.14, is unusual. The tertiary N is protected by a methyl group and is not expected to be available to bridge another iron. Even if the methyl group were removed it would still have a repeat unit of mass 183, 36 mass units higher than that observed. Each of the higher MW peaks is an iron containing compound, as confirmed by their isotopic distribution. MS/MS experiments have only been performed on the M+ 280 peak, so composition of the repeat unit is unknown.

Foffani and co-workers[61] have previously reported the fragmentation pattern for $Fe(NO)_2(CO)_2$. The spectrum was obtained with a collision energy of 50 eV. A cascading pattern was observed including ions such as $Fe(NO)_2(CO)_2^+$ (large), $Fe(NO)_2(CO)^+$ (2nd largest), $Fe(NO)(CO)_2^+$ (v.small), $Fe(NO)_2^+$ (small),$Fe(NO)(CO)^+$ (med), $Fe(CO)_2^+$

(v.small), $Fe(NO)^+$ (med), $Fe(CO)^+$ (large), FeN^+ (med), Fe^+ (largest), NO^+ (large), CO^+ (large). The ms/ms experiments were performed on compounds **1 - 5** with more gentle collision conditions than Foffani's work (collision energies no greater than 35 eV, as compared to 50 eV for Foffani). The spectra obtained for compounds **1 - 5** obviously do not have the same degree of fragmentation with the lower collision energy, but the spectra in Figures 2.20 - 2.27 still provide useful information. We observe the characteristic losses of NO and Im ligands for each compound, the fragment ion MW's of which are listed in Table 2.17.

The ESCI technique was used on the $Fe(NO)_2(1\text{-MeIm})_2$ reaction mixture to try to gain insight into the decomposition of the $Fe(NO)_2(L)_2$ set of compounds. The dark green mixture was exposed to air and allowed to react, after which, samples of the solution were injected at timed intervals. Figure 2.14 shows the initial spectra before exposure to air. Upon exposure, the solution immediately turned to a clear brown solution. The spectra obtained (Figure 2.28) shows the 280 peak remains the dominant ion peak, with many new peaks appearing lower than 280. Higher MW iron containing peaks are still visible at 427 and 574, but much lower intensity than the 280 peak.

After 5 minutes (Figure 2.29), the solution became cloudy and took on a more orange colour. The M+ 280 was still relatively large, but is no longer the dominant peak. The 165 ion became the largest peak, which corresponds to the 1-MeIm dimer. There are no peaks in the spectrum that are observed as daughters of the 280 peak. An unknown peak appears at 348, almost of the same intensity as the 280 ion. A small peak at 473 is still observed, while the peak at 574 has disappeared.

At seven minutes (Figure 2.30), the solution had cleared and a precipitate settled to the bottom of the flask. The ions of mass greater than 400 are no longer discernable above the baseline, and the spectrum is still complex. A large non-iron peak is visible at 105 and becomes the dominant peak. The 280 ion peak is very small and the 165 peak is just slightly smaller than the 105 peak.

After 10 minutes (Figure 2.31), the solution became almost clear, with an orange precipitate covering the bottom of the flask. The solution contains mainly protonated imidazole ligand. A small amount of the dimer 1-MeIm dimer appears at 165. An unknown peak also remains at m/z 105, but much smaller than m/z 165.

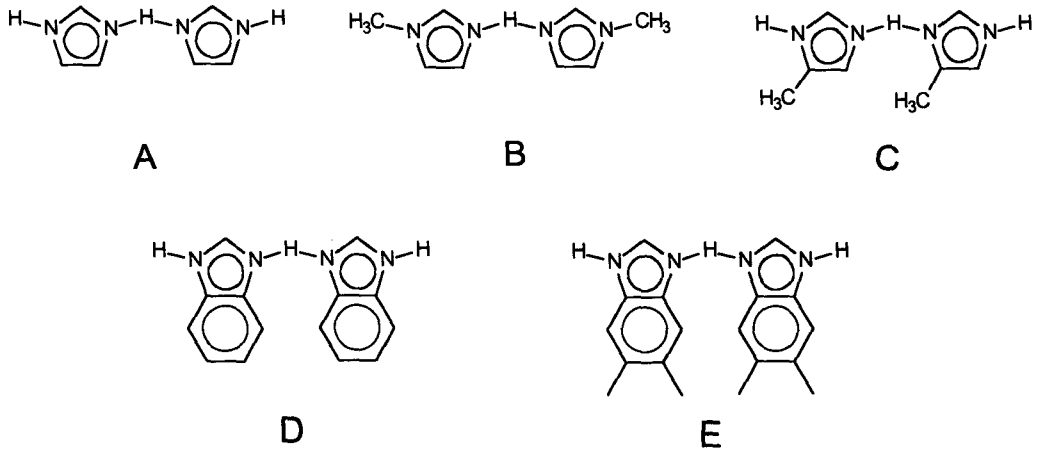
These experiments show no characteristic losses of NO and ligand, as found by ms/ms experiments. This infers that the reaction is not proceeding by way of a dissociative (S_N1 type) substitution mechanism and therefore most likely proceeds *via* an associative (S_N2 type) pathway. There are no soluble iron containing compounds in solution after 7 - 10 minutes, which leaves mainly the 1-MeIm ligand (1-MeImH$^+$, m/z 83) and the dimer complex (shown in Scheme 2.6 B, m/z 165) as the major species in the spectra. The colour of the precipitate after 7 - 10 minutes is orange, and may be an iron oxide. It is thought that upon exposure of the solution to air, oxygen addition occurs at the iron center to produce a bimolecular intermediate compound. A molecular weight peak reflecting a species of this nature has not yet been deciphered in the spectra.

Table 2.14. Parent ion peaks for iron nitrosyl imidazole compounds.

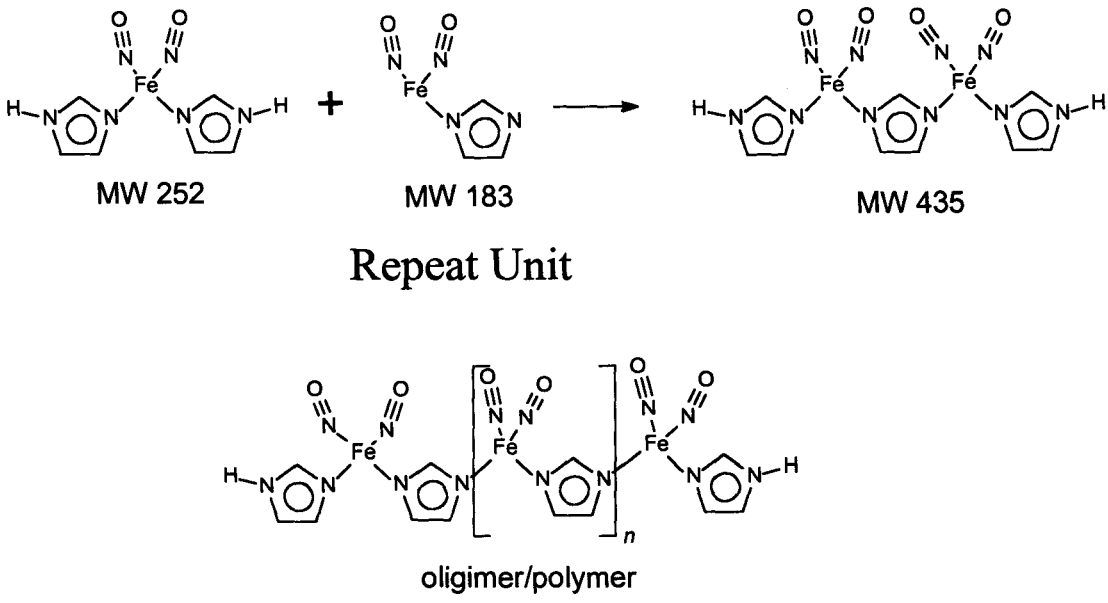
Compound	M+ (Da/e)
1 $Fe(NO)_2(imidazole)_2$	252.0
2 $Fe(NO)_2(1\text{-}MeIm)_2$	280.0
3 $Fe(NO)_2(4\text{-}MeIm)_2$	279.9
4 $Fe(NO)_2(Benzimidaole)_2$	352.1
5 $Fe(NO)_2(5,6\text{-}dimethylbenzim)_2$	408.2

Table 2.15. Imidazole dimers in found in mass spectra.

Molecular Weights of Imidazole Dimers		
Original compound	Symbol	Molecular Weight
1 $Fe(NO)_2(imidazole)_2$	**A**	137 (large)
2 $Fe(NO)_2(1\text{-}MeIm)_2$	**B**	165 (large)
3 $Fe(NO)_2(4\text{-}MeIm)_2$	**C**	165 (v.small)
4 $Fe(NO)_2(Benzimidaole)_2$	**D**	237 (v.small)
5 $Fe(NO)_2(5,6\text{-}dimethylbenzim)_2$	**E**	293 (v.small)



Scheme 2.6. Proposed structures of imidazole dimers detected in mass spectrometer.



Scheme 2.7. Proposed structures of oligomers detected in mass spectrometer.

Table 2.16. High MW ions found in Mass spectra of iron dinitrosyl imidazole compounds.

Compound	MW Peaks Observed	MW Repeat Unit
1 $Fe(NO)_2$(imidazole)$_2$	252, 435, 618, 801	183
2 $Fe(NO)_2$(1-MeIm)$_2$	280, 427, 574, 721	147
3 $Fe(NO)_2$(4-MeIm)$_2$	280, 477, 674, 871, 1068	197
4 $Fe(NO)_2$(Benzimidaole)$_2$	352, 585, 818, 1051, 1284	233
5 $Fe(NO)_2$(5,6-dimethylbenzim)$_2$	408, 669, 930	261

Table 2.17. MS/MS of iron dinitrosyl imidazole compounds.

Compound	Daughters of	Observed Peaks
1 $Fe(NO)_2(imidazole)_2$	252	222 (-NO), 191 (-2NO), 184 (-Im), 154 (-NO, Im)
2 $Fe(NO)_2(1\text{-MeIm})_2$	280	280 (M+), 250 (-NO), 220 (-2NO), 168 (-NO, 1-MeIm)
3 $Fe(NO)_2(4\text{-MeIm})_2$	280	280 (M+), 250 (-NO), 220 (-2NO), 168 (-NO, 1-MeIm)
	477	477 (M+), 447 (-NO), 417 (-2NO), 395 (-4-MeIm), 365 (-NO, 4-MeIm), 335 (-2NO, 4-MeIm)
4 $Fe(NO)_2(Benzimidaole)_2$	352	322 (-NO), 292 (-2NO), 234 (-benzim), 204 (-NO, benzim)
	585	585 (M+), 555 (-NO), 525 (-2NO), 477 (-benzim), 437 (-NO, benzim)
5 $Fe(NO)_2(5,6\text{-dimethylbenzim})_2$	408	408 (M+), 378 (-NO), 348 (-2NO), 262 *, 232 (-5,6dimethylbenz), 202 (-NO, -5,6dimethylbenz)

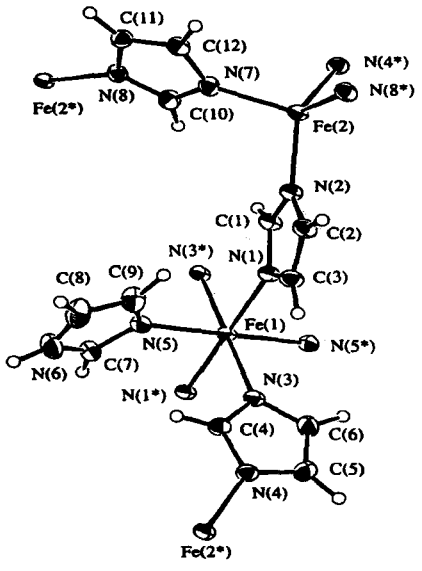


Figure 2.19. Ortep diagram of $[Fe_3(imid)_6(imidH)_2]_x$

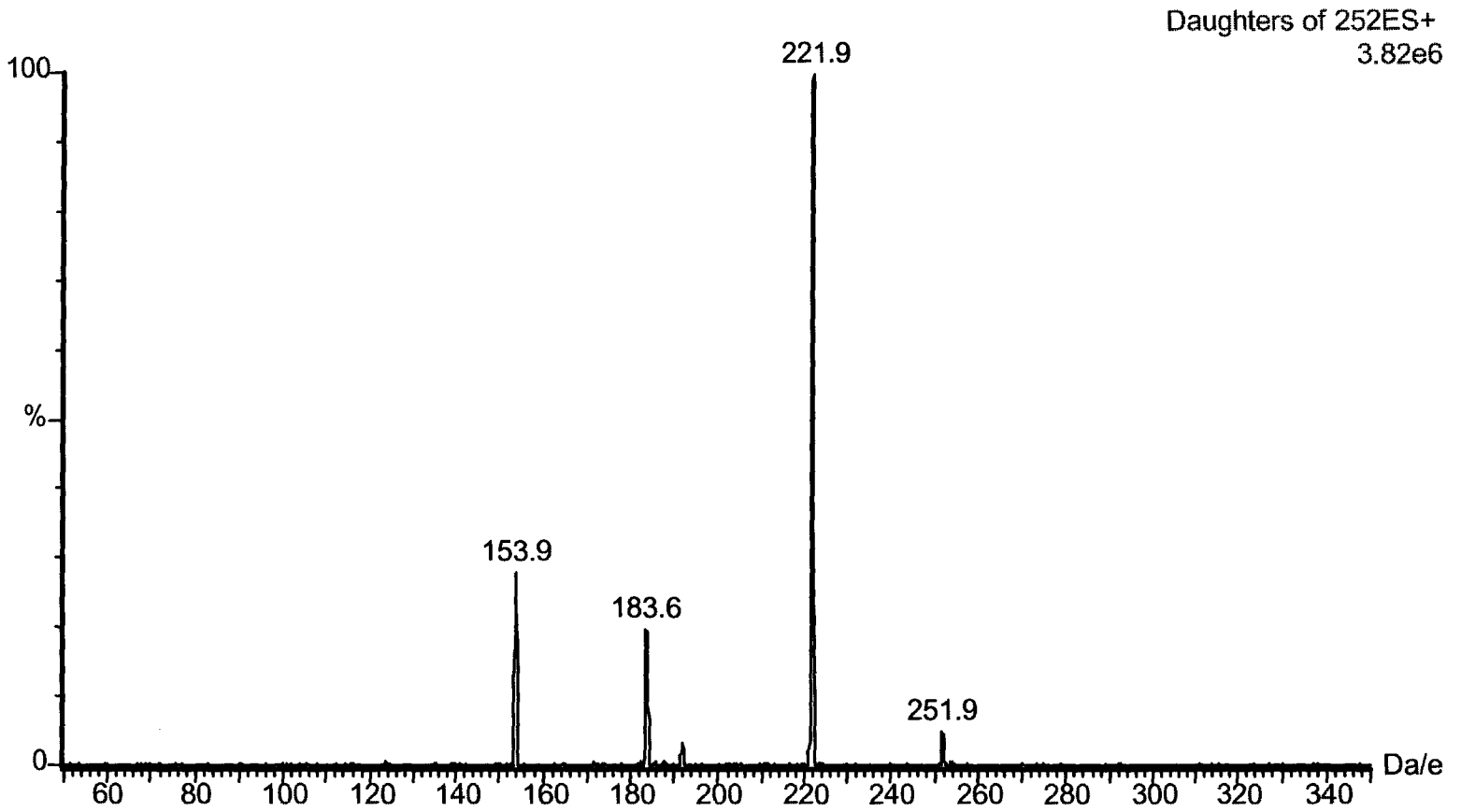


Figure 2.20. Daughters of $Fe(NO)_2(imidazole)_2^+$ 252 ion

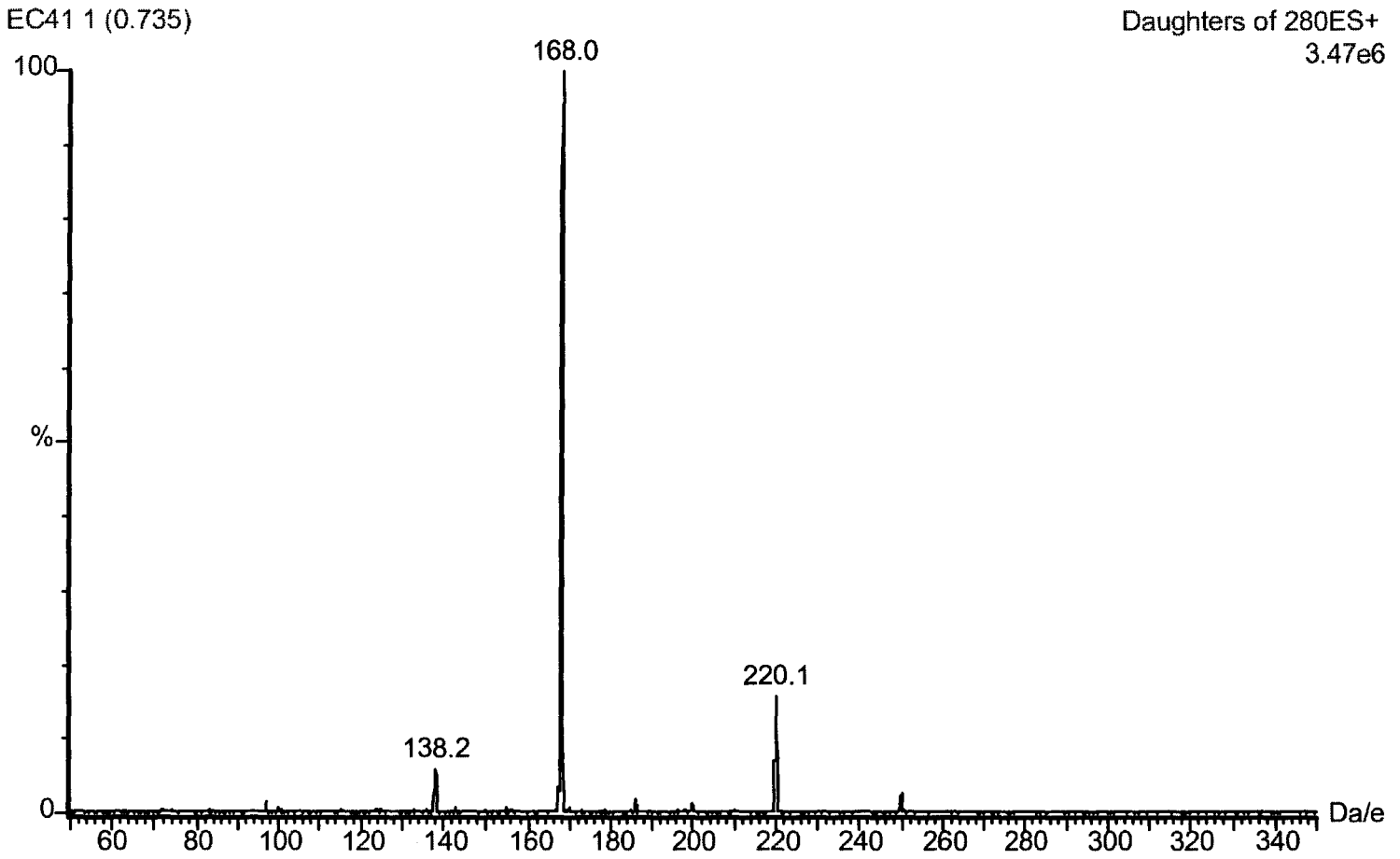


Figure 2.21. Daughters of $Fe(NO)_2(1\text{-MeIm})_2^+$ 280 ion

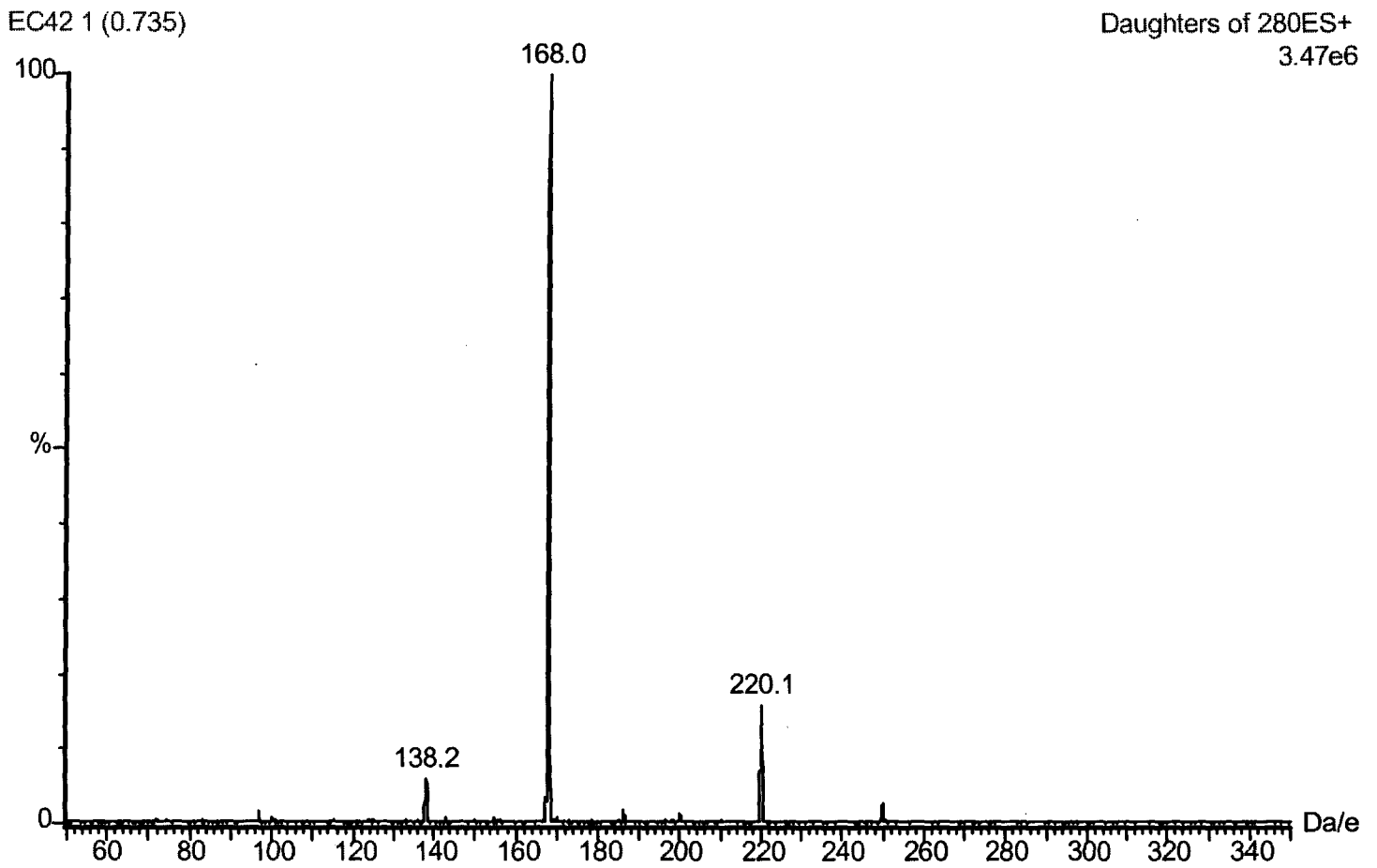


Figure 2.22. Daughters of $Fe(NO)_2(4\text{-MeIm})_2^+$ 280 ion

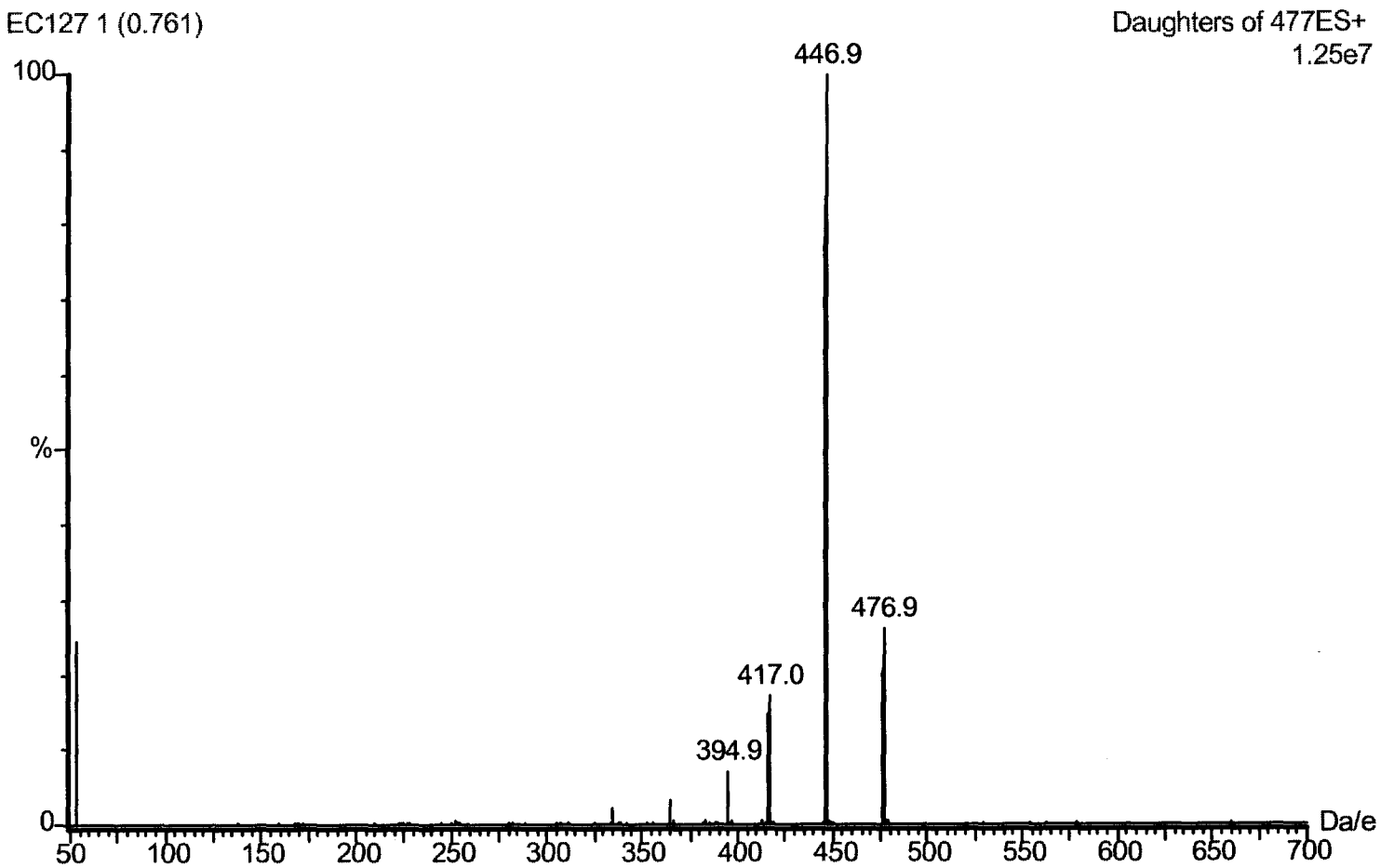


Figure 2.23. Daughters of $Fe(NO)_2(4\text{-MeIm})_2^+$ 477 ion

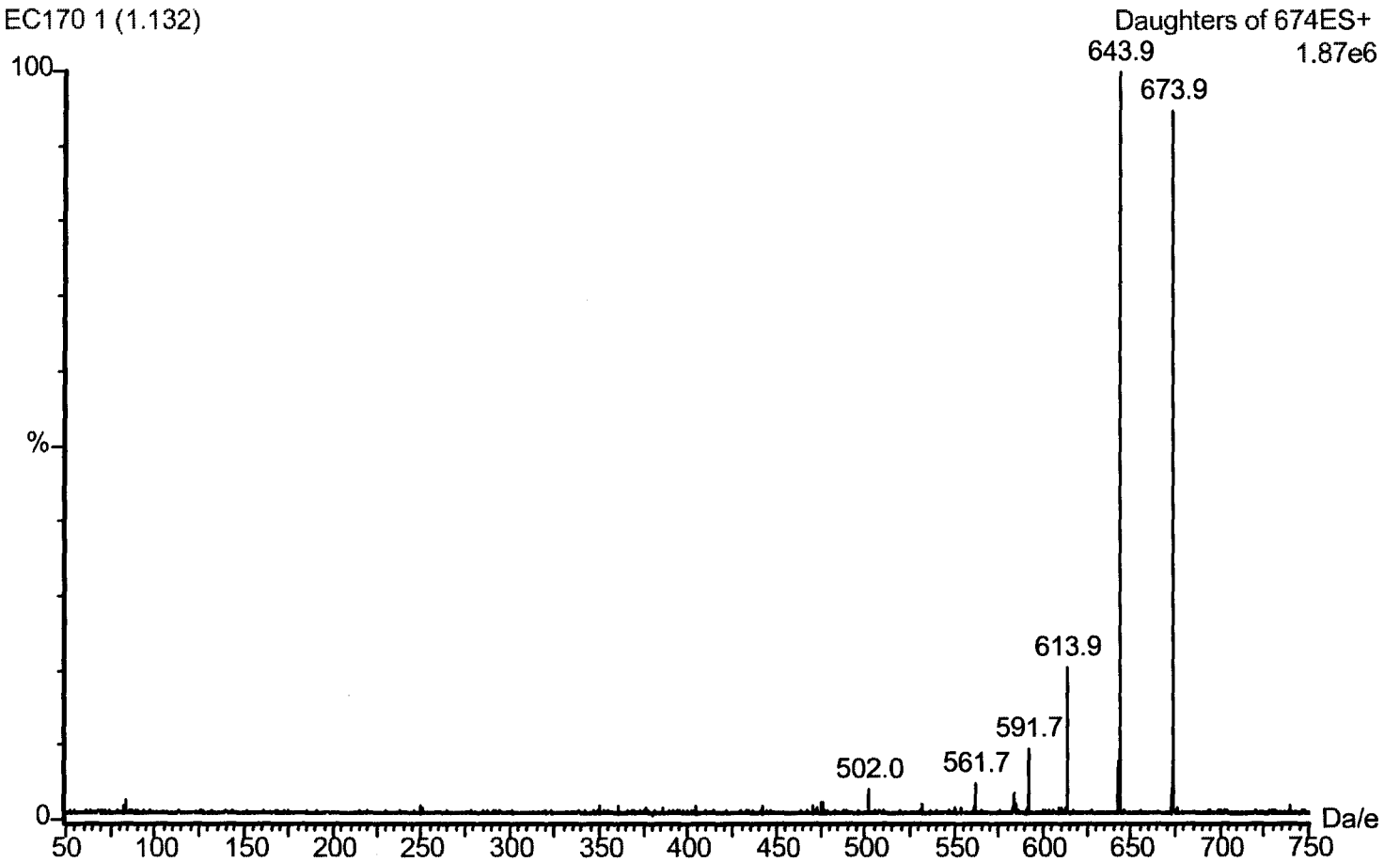


Figure 2.24. Daughters of $Fe(NO)_2(4\text{-MeIm})_2^+$ 674 ion

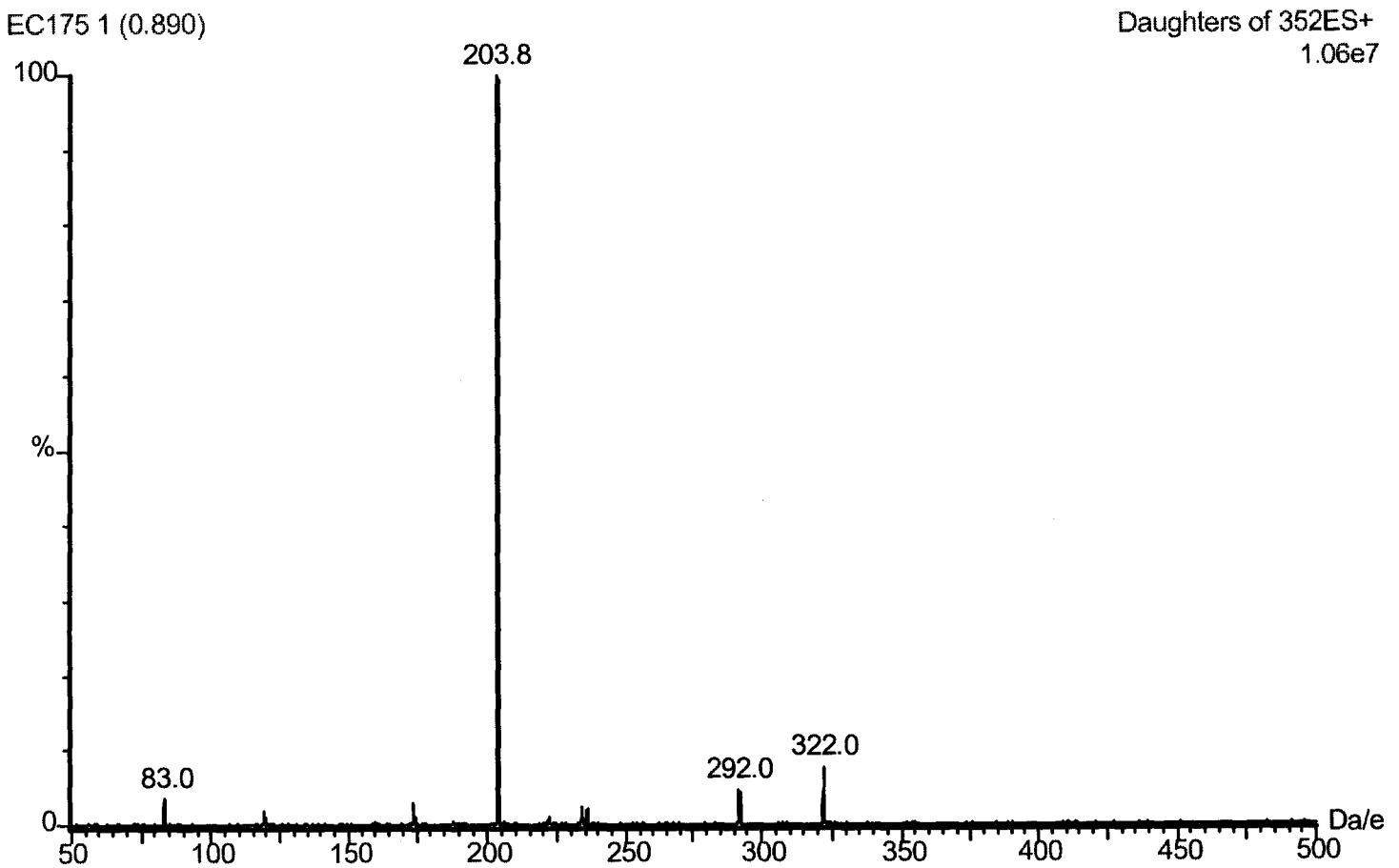


Figure 2.25. Daughters of $Fe(NO)_2(benzimidazole)_2^+$ 352 ion

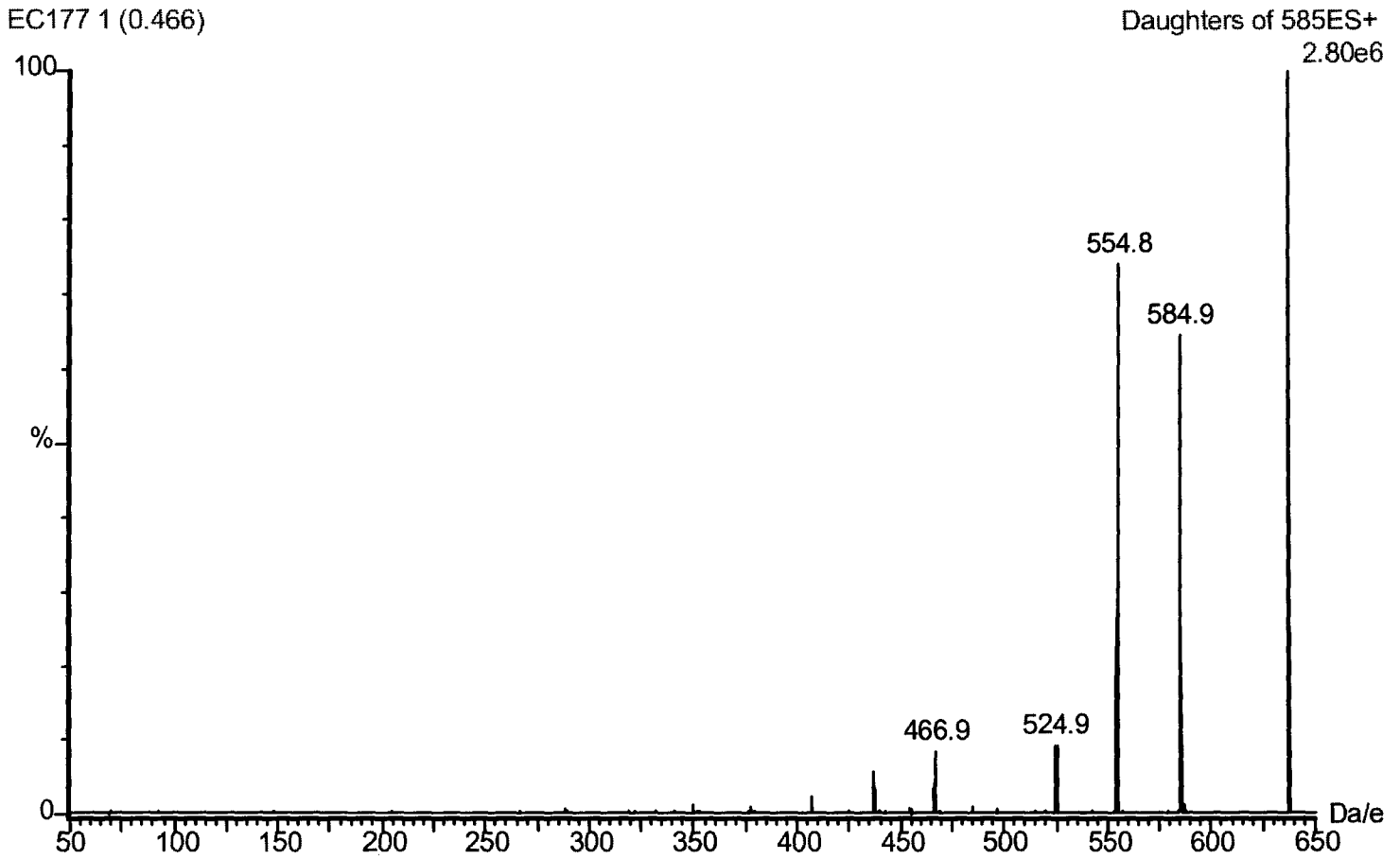


Figure 2.26. Daughters of $Fe(NO)_2(benzimidazole)_2^+$ 585 ion

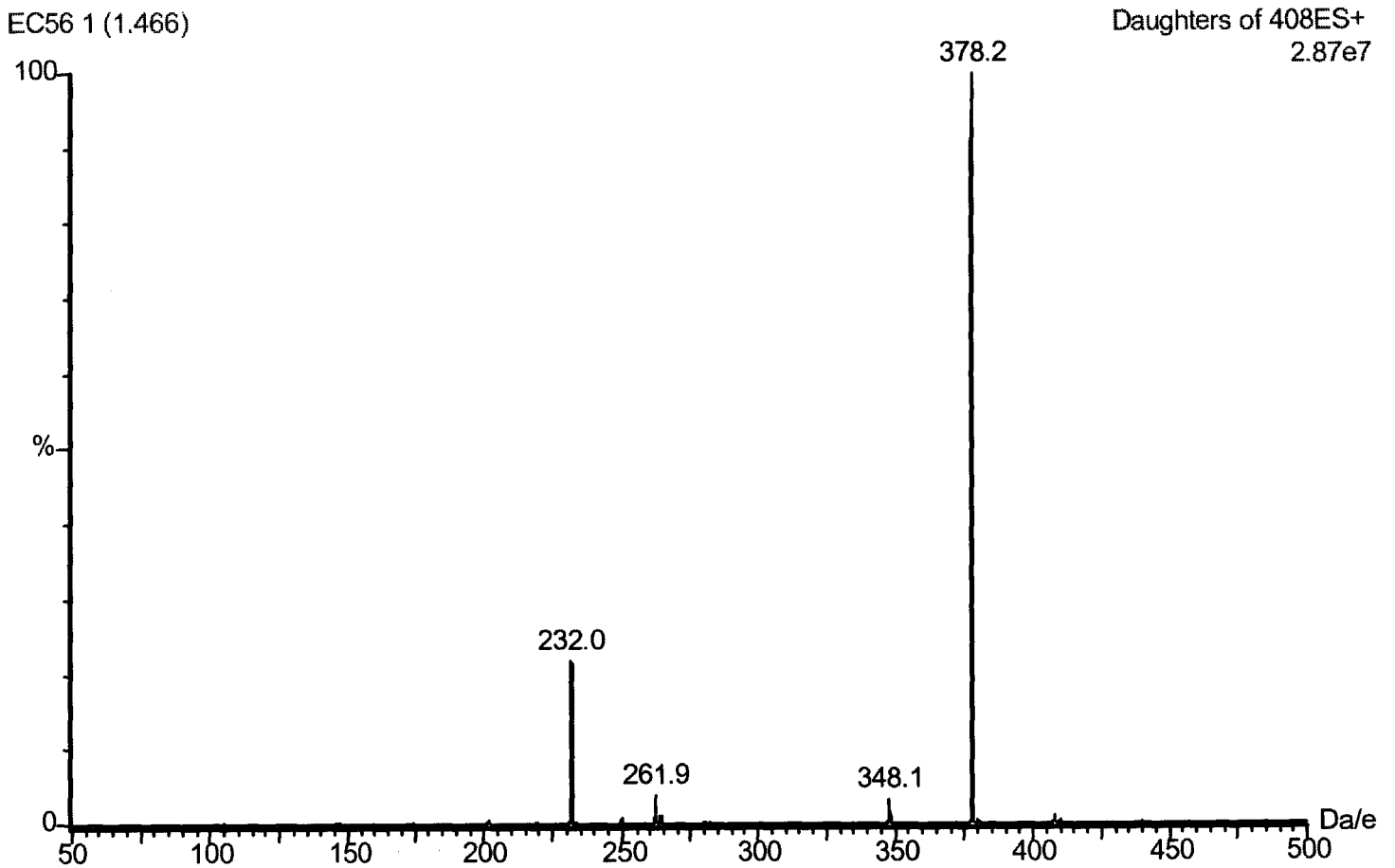


Figure 2.27. Daughters of $Fe(NO)_2$(5,6-dimethylbenzimidazole)$_2^+$ 408 ion

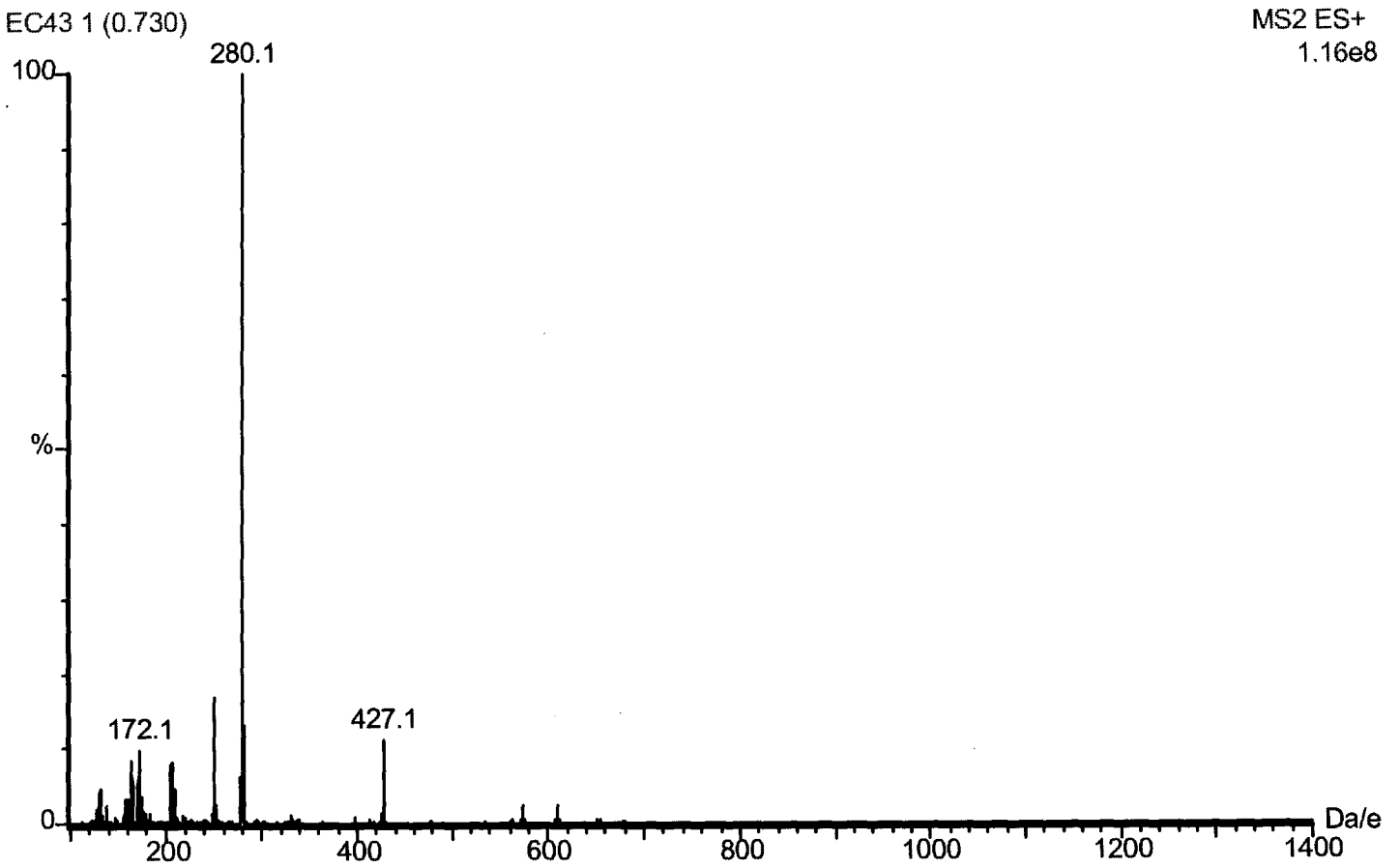


Figure 2.28. MS Spectrum of $Fe(NO)_2(1\text{-MeIm})_2$ immediately after exposure to air.

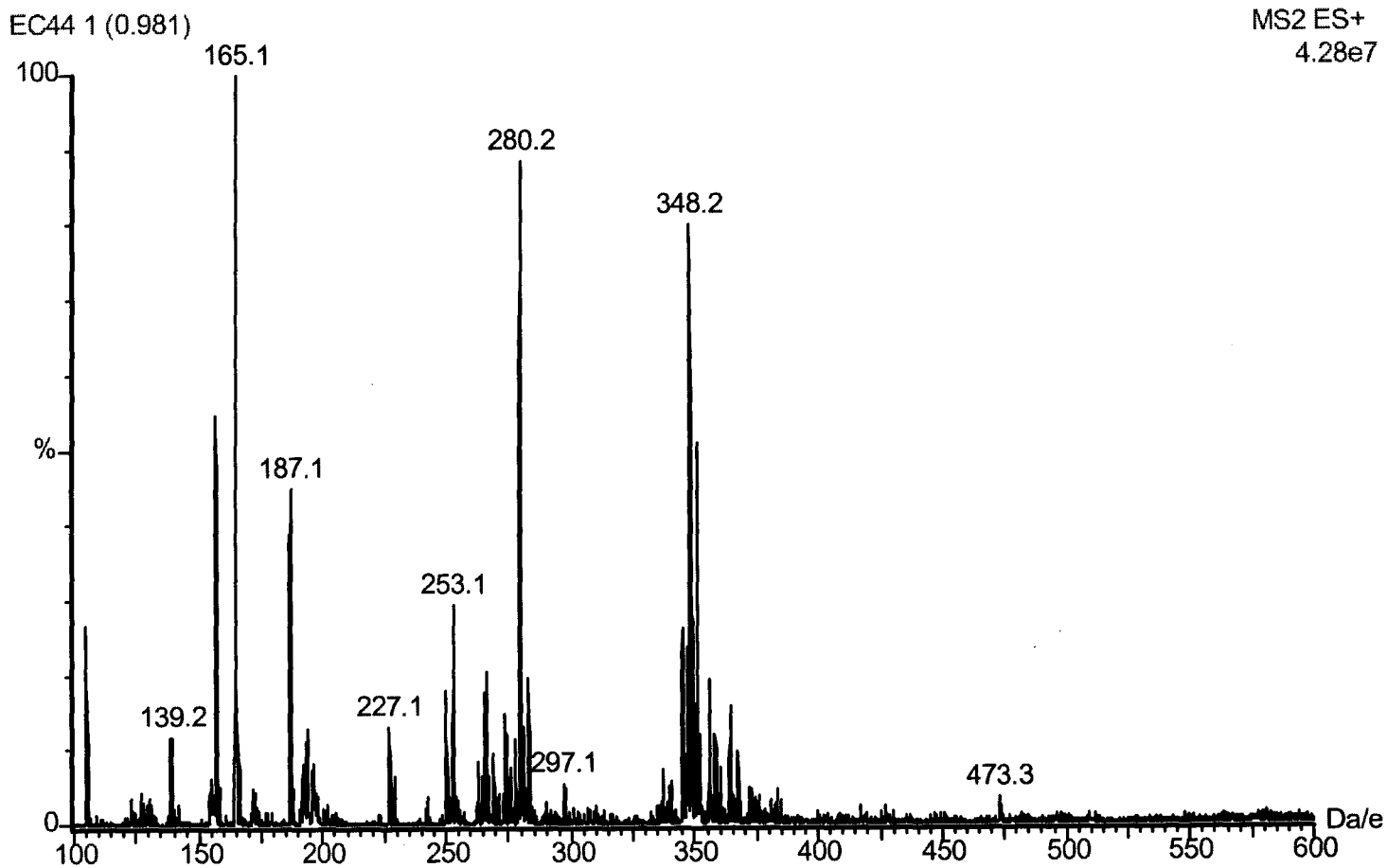


Figure 2.29. MS Spectrum of $Fe(NO)_2(1\text{-MeIm})_2$, 5 minutes after exposure to air.

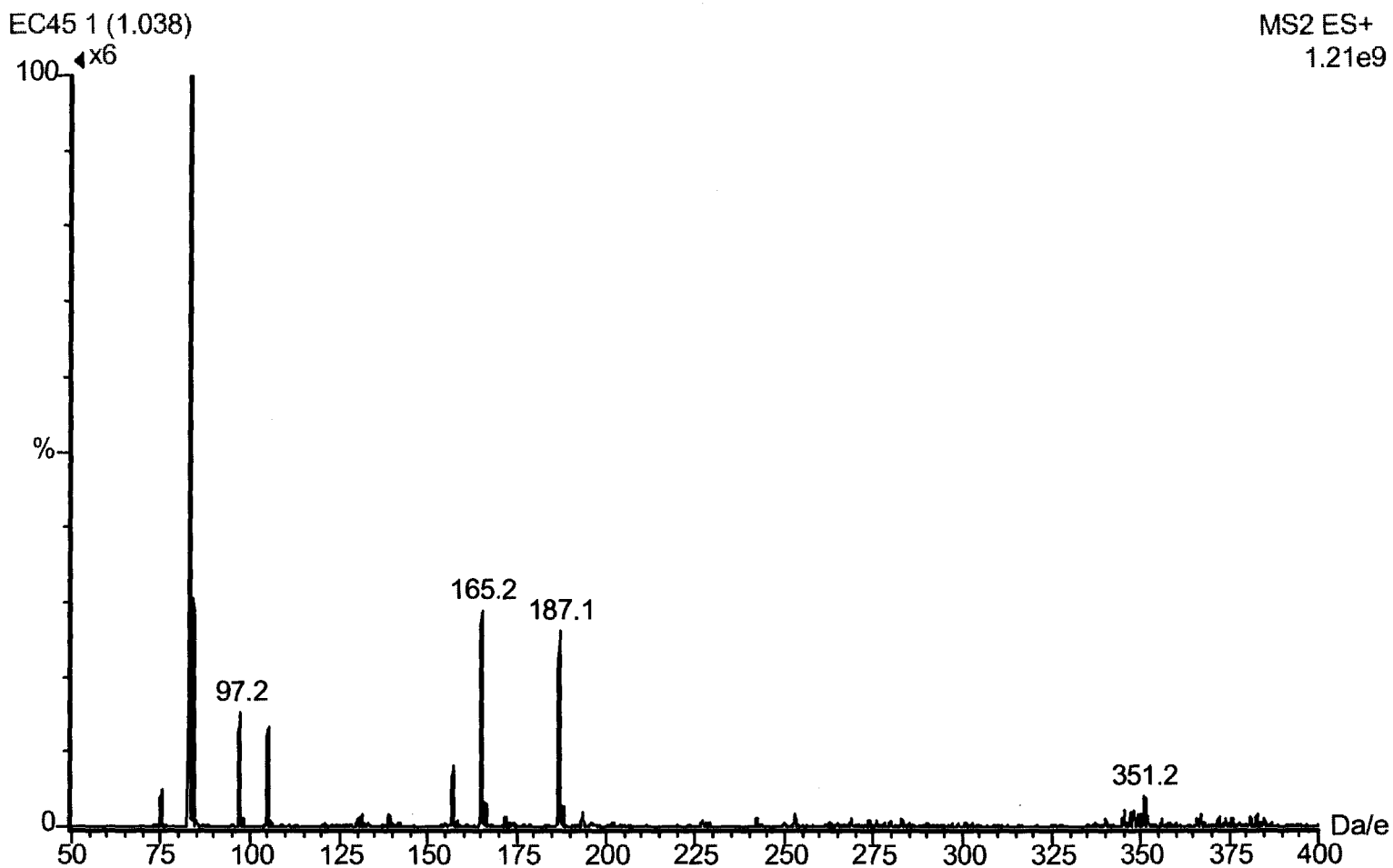


Figure 2.30. MS Spectrum of $Fe(NO)_2(1\text{-MeIm})_2$, 7 minutes after exposure to air.

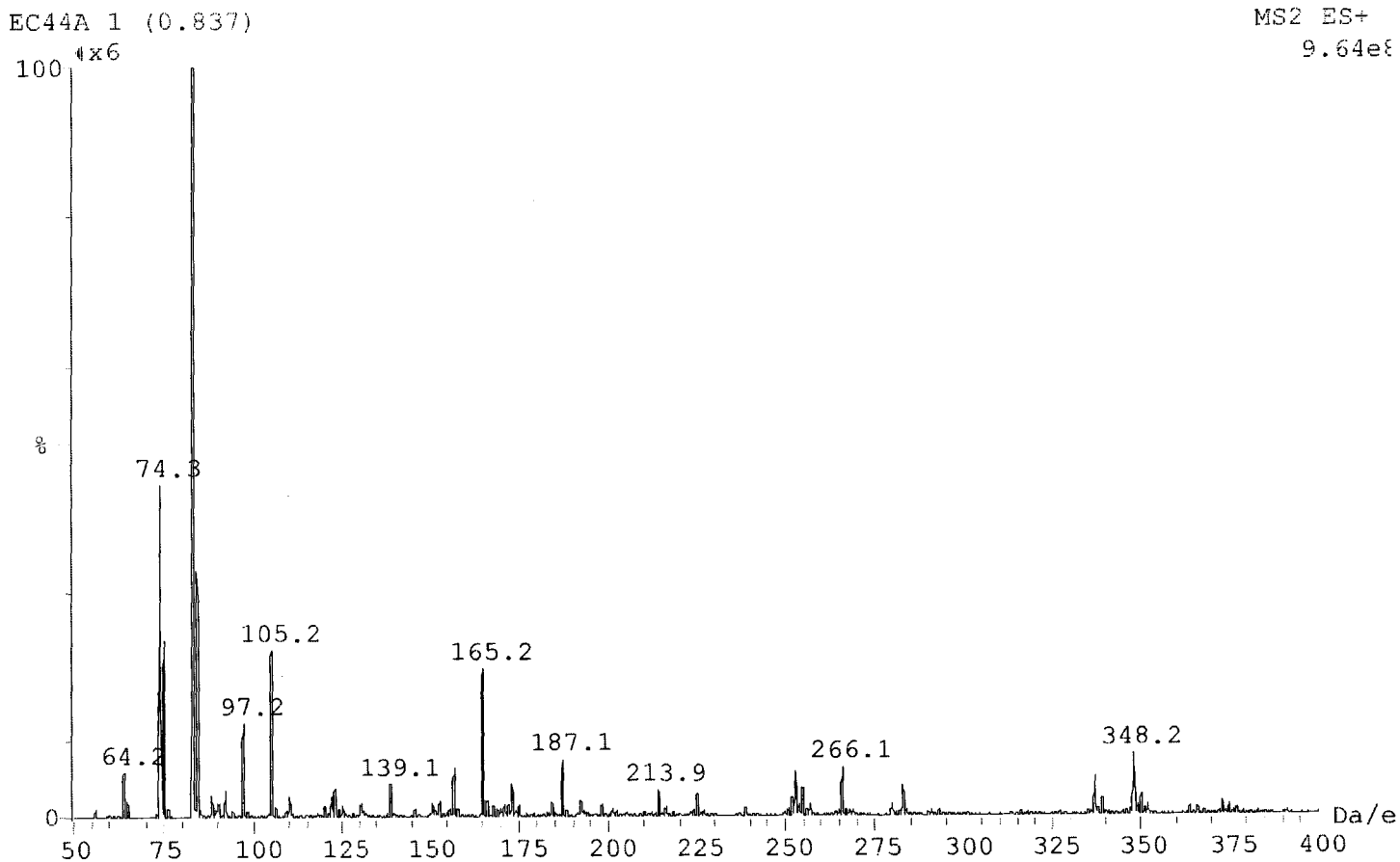


Figure 2.31. MS Spectrum of $Fe(NO)_2(1\text{-MeIm})_2$, 10 minutes after exposure to air.

3. Experimental

Tetrahydrofuran (THF) was refluxed over sodium/benzophenone until the mixture became blue/purple. The THF was then distilled and collected under inert nitrogen atmosphere. Diethylether was refluxed over sodium/benzophenone until the mixture became blue. The ether was then distilled and collected under inert nitrogen atmosphere. Dichloromethane and methanol were both refluxed over calcium hydride (CaH_2) for 24hrs. Dichloromethane and MeOH were then distilled and collected under inert nitrogen atmosphere. Pentacarbonyliron(o), imidazole, 1-methylimidazole, 4-methylimidazole, benzimidazole, 5,6-dimethylbenzimidazole and sodium metal were purchased from Sigma-Aldrich Chemicals and used without further purification. Sodium nitrite was purchased from Fischer Scientific and used without further purification.

Dinitrosyldicarbonyliron(o) and subsequent imidazole complexes were air sensitive. Manipulations were carried out either in a glove bag or in a two station dry box (Innovative Technology), both purged with nitrogen dried by passing through a "Lab Clear" gas drying bottle .

3.1 FT-IR Spectroscopy

IR spectra were recorded on a Bio-Rad FTS-40 spectrometer as KBr pellets or using a CaF_2 solution cell. Solution IR were performed using 2:1 reaction mixtures of the appropriate imidazole ligand and $Fe(NO)_2(CO)_2$, in THF. The IR spectrum for

$Fe(NO)_2(CO)_2$ was obtained by dissolving it in ether and using a NaCl solution cell.

3.2 Nuclear Magnetic Resonance (NMR)

All NMR spectra were recorded on either a Bruker AC-200 (^1H 200MHz, ^{13}C 50MHz) or AC-300 (^1H 300MHz, ^{13}C 75MHz) spectrometer. Samples were prepared under nitrogen in a glove-bag by performing the reactions in deuterated methanol, in a reaction flask fitted with a young valve and a side arm with an NMR tube attached by a 1/4" Swagelok ultra-torr connector. After CO evolution subsided, the mixture was poured through the side-arm, into the NMR tube, frozen and flame sealed. $Fe(NO)_2(CO)_2$ was filtered through glass wool and washed with one ampule of deuterated MeOH. Following this was the imidazole ligand, dissolved in one ampule of d-MeOH.

3.3 Electron Paramagnetic Resonance Spectroscopy (EPR)

All EPR spectra were recorded on a Bruker EMX 8/2.7 spectrometer, operating at a frequency of 9.4 GHz (X–band) with a magnetic field modulation of 100 kHz and equipped with a variable-temperature device. Samples were prepared under nitrogen in a glove bag. A solution of $Fe(NO)_2(CO)_2$ dissolved in THF was added through a glass wool filter to a reaction flask fitted with a young valve and a side arm with a quartz micro-EPR tube. A 2 molar equivalent of the appropriate imidazole ligand , dissolved in THF, was then added through a glass wool filter to the reaction flask. Spectra were obtained immediately.

3.4 X-ray crystallography

X-ray crystallographic data for **2** were collected from a single crystal sample, which had been place on a glass fibre, mounted 6mm above a brass pin, using paraffin oil as the adhesive. The X-ray crystallographic data for **6** were collected from a single crystal sample, which had been mounted on a glass fibre, 6mm above a brass pin, using epoxide glue as the adhesive. Both data sets were collected at -60°C, using a P4 Siemens diffractometer, equipped with a Siemens SMART 1K Charged-Coupled Device (CCD) Area Detector (using the program SMART) and a rotating anode using graphite-monochromated Mo-Kalpha radiation (lambda = 0.71073 A). The crystal-to-diffractometer distance was 3.9991 cm and the data collection was carried out in 512 X512 pixel mode, utilizing 2 x 2 pixel binning. The initial unit cell parameters were determined by least-squares fit of the angular settings of the strong reflections, collected by a 4.4 degree scan in 15 frames over three different parts of reciprocal space (45 frames total). After one complete hemisphere of data collection, the first frames were recollected in order to improve the decay corrections analysis. Processing was carried out by the use of the program SAINT, which applied Lorentz and polarization corrections to three-dimensionally integrated diffraction spots. The program SADABS was utilized for the scaling of diffraction data, the application of decay correction, and an empirical absorption correction based on redundant reflections.

The structures of **2** and **6** were solved by using the direct methods procedure in the Siemens SHELXTL program library, and refined by full-matrix least squares methods with anisotropic parameters for all atoms, except the methyl hydrogens at the C4 and C8

positions of **2**. The hydrogens of the C4 and C8 atoms of **2** were generated at calculated positions, with thermal parameters based on the carbons to which they are attached.

3.5Mass Spectra

Pneumatically assisted electrospray (ES) was performed with either DCM or a mixture of 90/10 dichloromethane/methanol as the mobile phase at a flow rate of 10μL/min employing a Brownlee Microgradient syringe pump. Samples were prepared by reacting 10μl (8.727 x 10^{-5} mol) $Fe(NO)_2(CO)_2$ with 1.7454 x 10^{-4} mol of imidazole ligand in either 10mL DCM or MeOH and were introduced by loop injection (10μL). Data was acquired in MCA mode. Full scan positive ion ES experiments (MS and MS/MS) were performed with a Micromass Quattro-LC triple quadrupole instrument. The PEEK tubing and fittings were replaced with either stainless steel or teflon. A Rheodyne 7125 HPLC injection valve was connected to the ES probe with ~10cm of teflon tubing to allow sample introduction to take place as close as possible to the exit of the stainless steel ES capillary. Operating parameters were as follows: source temperature 80°C, cone voltage (CV) 5 - 15V (normally 35V or greater) and a capillary voltage of 4 - 4.5 kV (normally 3 - 3.5kV). Argon was used as the collision gas for MS/MS experiments at a gas cell pressure of ~ 2 x 10^{-3} mBar.

3.6 Synthesis of Complexes

Synthesis of Dinitrosyldicarbonyliron(0)

Dinitrosyldicarbonyliron(0) was synthesized by a modified method of Seel.[62] Twenty five milliliters of Ironpentacarbonyl (0.20 mol) was dissolved in 400mL of methanol, along with 10g (0.44 mol) sodium metal and 17g (0.25 mol) sodium nitrite. The solution was refluxed until the distillate no longer showed a yellow colour. The methanol was distilled off at 70°C to leave a dry yellow product, $Na[Fe(NO)(CO)_3]$. 400mL of distilled H_2O was added and 17g (0.25 mol) of sodium nitrite. The solution was purged with a slow flow of CO_2 and the yellow/orange gas evolved was collected in a series of 3 U-tubes as a brick red solid, at -78°C in a dry ice/acetone bath. The yield was 20g (60%). MW = 171.88g/mol; d = 1.56 g/cm^3; m.p. = 21.6 °C; IR (in ether): ν(NO): 1810 cm^{-1}, 1767 cm^{-1}; ν(CO) : 2087 cm^{-1}, 2038 cm^{-1}.

Synthesis of Diimidazoledinitrosyliron(0) (1)

$Fe(NO)_2(CO)_2$ (0.1mL, 8.727 x 10^{-3} mol) was added to a solution of 0.10g (0.01745 mol) of imidazole dissolved in 1mL of ether. Gas evolved, and within two minutes the solution turned from a red to a green colour. The solvent was removed by reduced pressure. The solid was washed three times with ether and decanted each time. After the final wash, the solid was dried under reduced pressure at room temperature. Yield 68 %; MW 250g/mol ; M+ 250 m/z, 222 (M+ -NO), 191 (M+ - 2NO), 184 (M+ - Im), 154 (M+ -NO, Im); IR:$\nu_{(NO)}$ 1680, 1622 cm^{-1}; EPR: g 2.0344, a_{n1} 3.3, a_{n2} 2.4, 2 X a_{n3} 2.1 G.

Synthesis of Di(1-methylimidazole)dinitrosyliron(0) (2)

$Fe(NO)_2(CO)_2$ (0.1mL, 8.727 x 10^{-3} mol) was added to a solution of 0.120mL (0.01745 mol) of 1-methylimidazole dissolved in 1mL of ether. Gas evolved, and within two minutes the solution turned from a red to a green colour. The solvent was removed by reduced pressure. The solid was washed three times with ether and decanted each time. After the final wash, the solid was dried at reduced pressure and at room temperature. Yield 87 %; MW 280 g/mol ; M+ 280 m/z, 250 (M+ - NO), 220 (M+ - 2NO), 168 (M+ - NO, 1-MeIm) ; IR $\nu_{(NO)}$ 1673, 1616 cm^{-1}; EPR g 2.0275, 2 X a_{n1} 2.9, 2 X a_{n2} 2.6 G.

Synthesis of Di(4-methylimidazole)dinitrosyliron(0) (3)

$Fe(NO)_2(CO)_2$ (0.1mL, 8.727 x 10^{-3} mol) was added to a solution of 0.120g (0.01745 mol) of 4-methylimidazole dissolved in 1ml of ether. Gas evolved, and within two minutes the solution turned from a red to a green colour. The solvent was removed by reduced pressure. The solid was washed three times with ether and decanted each time. After the final wash, the solid was dried under reduced pressure at room temperature. Yield 62 %; MW 280 g/mol; M+ 280 m/z, 250 (M+ - NO), 220 (M+ - 2NO), 168 (M+ - NO, 1-MeIm), M+ 477 m/z, 477 (M+), 447 (M+ - NO), 417 (M+ - 2NO), 395 (M+ - 4-MeIm), 365 (M+ - NO, 4-MeIm), 335 (M+ - 2NO, 4-MeIm); IR $\nu_{(NO)}$ 1677, 1620 cm^{-1}; EPR g 2.0336, a_{n1} 3.1, a_{n2} 2.5, 2 X a_{n3} 2.2 G.

Synthesis of Di(benzimidazole)dinitrosyliron(0) (4)

$Fe(NO)_2(CO)_2$ (0.1mL, 8.727 x 10^{-3} mol) was added to a solution of 0.173g (0.01745 mol) of benzimidazole dissolved in 1mL of THF. Gas evolved, and within two minutes the solution turned from a red to a green colour. The solvent was removed by reduced pressure. The solid was washed three times with ether and decanted each time. After the final wash, the solid was dried under reduced pressure at room temperature. Yield 68%; MW 352 g/mol ; M+ 352 m/z, 322 (M+ - NO), 292 (M+ - 2NO), 234 (M+ - benzim), 204 (M+ - NO, benzim), 585 m/z (M+), 555 (M+ - NO), 525 (M+ - 2NO), 477 (M+ - benzim), 437 (M+ - NO, benzim); IR $\nu_{(NO)}$ 1682, 1625 cm^{-1}; EPR g 2.0341, a_{n1} 3.8, a_{n2} 2.4, 2 X a_{n3} 1.9.

Synthesis of Di(5,6-dimethylbenzimidazole)dinitrosyliron(0) (5)

$Fe(NO)_2(CO)_2$ (0.1mL, 8.727 x 10^{-3} mol) was added to a solution of 0.213g (0.01745 mol) of 5,6-dimethylbenzimidazole dissolved in 1mL of THF. Gas evolved, and within two minutes the solution turned from a red to a green colour. The solvent was removed by reduced pressure. The solid was washed three times with ether and decanted each time. After the final wash, the solid was dried under reduced pressure at room temperature. Yield: 81 % ; MW: 408 g/mol; M+ 408 m/z, 378 (M+ - NO), 348 (M+ - 2NO), 262 *, 232 (M+ - 5,6dimethylbenz), 202 (M+ - NO, -5,6dimethylbenz); IR:$\nu_{(NO)}$ 1683, 1625 cm^{-1}; EPR g 2.0344, a_{n1} 3.9, 2 X a_{n2} 2.2.

Synthesis of dinitrosylcarbonyltriphenylphospineiron(0)

$Fe(NO)_2(CO)_2$ (0.45mL, 4.11 x 10^{-3} mol) was added *via* a syringe to a stirred solution of triphenylphosphine (1.11g, 4.23 x 10^{-3} mol) in diethylether (10 mL), in an Erlenmyer flask fitted with a rubber septum . The flask received a positive pressure of nitrogen via a syringe. The dark red solution was stirred overnight at room temperature. The solvent was removed under reduced pressure and the dried red solid was washed with methanol.

Synthesis of Dinitrosyl-bis(triphenylphosphine)iron(0). (6)

0.02 ml (1.23 x 10^{-4} mol) of 1-methylimidazole was added to a solution of 0.01g (1.23 x 10^{-4} mol) $Fe(NO)_2(CO)(PPh_3)$ dissolved in 5 ml of diethylether in a glass test tube. The red solution was stoppered and turned dark red/green after one day, during which, large cubic crystals formed. A dark red crystal was obtained which provided the X-ray crystal structure of **6**. Yield, IR and EPR were not performed.

FUTURE WORK and CONCLUSIONS

First, and foremost, research into the methods of purification of these compounds should be undertaken. State of the art vacuum line techniques, similar to that presented by Burford,[63] would provide an excellent vehicle for advancement of this field. Electrochemical studies should be performed to further support the mechanistic pathway presented. Formation of an Im^- species would provide almost conclusive results that the process does occur by a catalytic 17-electron electron transfer chain mechanism (ETC). Also, the nature of the colour change from green to brown may be by an electronic means and electrochemistry may help support this idea. It is believed that either a one electron oxidation to the 17 electron complex, or one electron reduction to the 18 electron complex is the driving force for the colour change by some species in solution. Constant voltage experiments on bulk solutions may provide the means for a colour change of the solution. MS/MS experiments must be performed on the m/z peaks of **2**. The repeat unit of 147 mass units observed for these peaks is an iron containing compound, but is 36 mass units less than the repeat unit observed for **1**, which should be the smallest repeat unit for the series.

The syntheses of the $Fe(NO)_2(L)_2$ [L = imidazole **1**, 1-methylimidazole (1-MeIm) **2**, 4-methylimidazole (4-MeIm) **3**, benzimidazole (benzim) **4**, and 5,6-dimethylbenzimidazole (56benzim) **5**] series of compounds open the door to further research of biologically relevant iron nitrosyl chemistry. One future goal, is to mimic NO

transport. Elegant studies performed by Doyle[64,65] and Kadish[66,67] have shown that the NO ligand may be removed from an iron or cobalt center of porphyrin complexes by oxidizing the metal center. The higher the oxidation state, the weaker the metal nitrosyl bond and the more readily NO is released. It may be a process similar to this that allows metal mediated transfer in the human body. The d^{10} iron nitrosyl compounds have very strong M-N bonds and will not easily relinquish NO. Oxidation of compounds **1 - 5** would only provoke further instability and so it is not likely that these complexes would be a good illustration of species that release NO. Complexes **1 - 5** may then be more representative of an iron molecule *after* receiving NO. The goal then is to create a molecule which would accept NO to create the final products **1 - 5**. The use of a series of iron carbonyl imidazole complexes of the form $Fe(CO)_3(L)_2$ seem a likely choice as receptors of NO gas bubbled through solution. Substitution of three CO ligands by two NO ligands would create the 18 electron complexes of **1 - 5**.

The chemical sensitivity of the $Fe(NO)_2(L)_2$ series of compounds has precluded purification and isolation of theses products. However, studies of reaction mixtures have elucidated the 17-electron ETC mechanistic pathway by which they are formed. Supporting evidence of the pathway is provided by IR, EPR and Mass spectroscopic studies. X-ray crystallography of **2** has shown that the four coordinate complexes are of a *pseudo*-tetrahedral geometry.

APPENDIX A

Table 1. Observed and calculated structure factors for 2

h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s
2	0	0	1274	1240	19	10	10	0	43	59	43	14	4	1	57	21	56	8	10	1	295	300	9	-17	3	2	212	215	12
4	0	0	2418	2331	37	12	10	0	12	79	11	16	4	1	64	85	52	10	10	1	257	257	13	-15	3	2	207	174	13
6	0	0	1512	1397	24	1	11	0	0	10	1	-15	5	1	263	258	7	12	10	1	150	143	15	-13	3	2	53	22	52
8	0	0	78	38	31	3	11	0	33	27	32	-13	5	1	175	173	12	-11	11	1	64	47	53	-11	3	2	570	562	7
10	0	0	1052	1054	22	5	11	0	580	576	7	-11	5	1	52	77	38	-9	11	1	74	70	42	-9	3	2	150	160	12
12	0	0	784	817	10	7	11	0	444	455	10	-9	5	1	666	665	6	-7	11	1	142	133	28	-7	3	2	422	426	5
14	0	0	0	62	1	9	11	0	45	70	44	-7	5	1	579	584	5	-5	11	1	183	183	11	-5	3	2	488	467	6
16	0	0	31	48	30	11	11	0	112	99	31	-5	5	1	727	729	6	-3	11	1	143	157	15	-3	3	2	154	155	7
1	1	0	365	368	3	0	12	0	88	129	37	-3	5	1	554	585	6	-1	11	1	173	184	12	-1	3	2	1146	1152	12
3	1	0	1907	1939	17	2	12	0	93	76	26	-1	5	1	333	359	7	1	11	1	116	68	17	1	3	2	1016	1008	6
5	1	0	747	742	6	4	12	0	0	5	1	1	5	1	253	244	6	3	11	1	260	260	11	3	3	2	109	71	9
7	1	0	291	322	5	6	12	0	35	78	34	3	5	1	1172	1247	14	5	11	1	85	17	43	5	3	2	393	365	4
9	1	0	200	184	11	8	12	0	55	61	54	5	5	1	849	866	7	7	11	1	0	34	1	7	3	2	43	10	42
11	1	0	62	29	43	1	13	0	0	40	1	7	5	1	931	941	7	9	11	1	0	4	1	9	3	2	115	118	11
13	1	0	133	167	14	3	13	0	263	275	11	9	5	1	98	45	16	11	11	1	0	5	1	11	3	2	384	393	7
15	1	0	93	65	51	5	13	0	242	222	10	11	5	1	260	253	7	-8	12	1	0	66	1	13	3	2	115	105	17
17	1	0	80	41	29	7	13	0	197	187	12	13	5	1	390	401	6	-6	12	1	174	165	13	15	3	2	0	9	1
0	2	0	892	862	22	0	14	0	0	27	1	15	5	1	197	197	9	-4	12	1	189	193	15	-16	4	2	114	84	22
2	2	0	2746	2703	18	2	14	0	0	47	1	-14	6	1	217	218	9	-2	12	1	282	288	8	-14	4	2	465	463	7
4	2	0	1220	1217	9	4	14	0	34	37	34	-12	6	1	141	139	12	0	12	1	168	129	19	-12	4	2	190	199	11
6	2	0	577	570	5	-17	1	1	264	263	10	-10	6	1	473	463	6	2	12	1	333	335	8	-10	4	2	461	467	6
8	2	0	1776	1770	14	-15	1	1	268	258	9	-8	6	1	250	257	9	4	12	1	81	84	27	-8	4	2	181	155	10
10	2	0	977	964	8	-13	1	1	118	111	18	-6	6	1	74	46	27	6	12	1	34	105	33	-6	4	2	192	171	7
12	2	0	81	53	25	-11	1	1	106	125	17	-4	6	1	877	859	7	8	12	1	259	262	10	-4	4	2	1011	983	7
14	2	0	156	153	13	-9	1	1	194	205	9	-2	6	1	639	622	12	-7	13	1	0	34	1	-2	4	2	839	875	10
16	2	0	29	46	28	-7	1	1	609	674	6	0	6	1	394	426	8	-5	13	1	0	32	1	0	4	2	1217	1197	9
1	3	0	1356	1299	10	-5	1	1	2354	2295	18	2	6	1	684	738	7	-3	13	1	77	101	34	2	4	2	1460	1416	11
3	3	0	933	888	6	-3	1	1	1628	1632	12	4	6	1	246	217	12	-1	13	1	62	61	61	4	4	2	79	83	16
5	3	0	241	215	9	-1	1	1	87	76	4	6	6	1	198	214	9	1	13	1	80	46	29	6	4	2	611	614	5
7	3	0	381	380	6	1	1	1	1447	1448	10	8	6	1	485	499	5	3	13	1	0	30	1	8	4	2	1239	1258	10
9	3	0	393	399	6	3	1	1	1799	1861	13	10	6	1	80	99	26	5	13	1	118	77	25	10	4	2	483	455	6
11	3	0	184	181	11	5	1	1	1619	1613	11	12	6	1	331	321	7	7	13	1	85	19	36	12	4	2	299	287	11
13	3	0	85	64	85	7	1	1	560	564	5	14	6	1	97	111	17	-4	14	1	90	135	26	14	4	2	90	138	24
15	3	0	250	250	10	9	1	1	192	179	7	-15	7	1	110	101	19	-2	14	1	198	203	15	16	4	2	95	67	27
17	3	0	63	31	57	11	1	1	177	148	12	-13	7	1	301	319	7	0	14	1	203	198	12	-15	5	2	199	194	10
0	4	0	1839	1760	20	13	1	1	359	348	7	-11	7	1	0	31	1	2	14	1	108	84	22	-13	5	2	0	21	1
2	4	0	1402	1371	16	15	1	1	455	443	8	-9	7	1	330	333	8	4	14	1	56	40	56	-11	5	2	47	57	46
4	4	0	253	262	6	17	1	1	230	216	11	-7	7	1	584	568	7	-16	0	2	105	135	32	-9	5	2	725	754	7
6	4	0	397	389	5	-16	2	1	77	48	38	-5	7	1	154	185	15	-14	0	2	226	199	31	-7	5	2	621	634	8
8	4	0	538	537	6	-14	2	1	113	100	22	-3	7	1	753	734	7	-12	0	2	329	324	10	-5	5	2	659	642	7
10	4	0	620	615	6	-12	2	1	384	408	10	-1	7	1	226	209	9	-10	0	2	500	479	9	-3	5	2	517	485	11
12	4	0	645	646	7	-10	2	1	614	627	6	1	7	1	764	745	8	-8	0	2	786	780	11	-1	5	2	600	603	5
14	4	0	140	128	15	-8	2	1	502	501	5	3	7	1	467	462	8	-6	0	2	547	516	11	1	5	2	562	574	8
16	4	0	166	191	14	-6	2	1	654	643	6	5	7	1	543	525	8	-4	0	2	774	804	9	3	5	2	1019	1026	8
1	5	0	546	515	5	-4	2	1	304	278	5	7	7	1	430	422	8	-2	0	2	3067	3055	27	5	5	2	134	126	24
3	5	0	321	290	6	-2	2	1	478	471	6	9	7	1	281	293	8	2	0	2	26	64	26	7	5	2	51	63	51
5	5	0	529	527	6	0	2	1	1004	1007	8	11	7	1	431	437	6	4	0	2	1176	1123	24	9	5	2	352	344	5
7	5	0	381	374	6	2	2	1	36	11	36	13	7	1	220	231	9	6	0	2	184	123	10	11	5	2	198	174	9
9	5	0	211	207	8	4	2	1	304	294	4	15	7	1	97	83	37	8	0	2	1372	1369	15	13	5	2	164	159	12
11	5	0	214	208	9	6	2	1	273	246	6	-14	8	1	181	174	14	10	0	2	1511	1542	17	15	5	2	168	156	12
13	5	0	0	22	1	8	2	1	398	404	6	-12	8	1	222	207	11	12	0	2	422	414	10	-14	6	2	190	201	10
15	5	0	231	220	9	10	2	1	637	626	6	-10	8	1	191	186	15	14	0	2	170	186	18	-12	6	2	460	460	6
0	6	0	388	326	7	12	2	1	109	99	18	-8	8	1	374	393	7	16	0	2	215	203	17	-10	6	2	234	237	7
2	6	0	706	698	9	14	2	1	141	143	21	-6	8	1	25	3	25	-17	1	2	49	38	49	-8	6	2	117	113	13
4	6	0	993	987	8	16	2	1	48	42	47	-4	8	1	369	377	7	-15	1	2	95	108	22	-6	6	2	388	375	6
6	6	0	0	23	1	-17	3	1	177	175	19	-2	8	1	966	989	15	-13	1	2	197	185	13	-4	6	2	310	317	6
8	6	0	710	728	6	-15	3	1	314	314	9	0	8	1	672	639	7	-11	1	2	210	206	10	-2	6	2	724	752	7
10	6	0	384	387	6	-13	3	1	209	213	10	2	8	1	194	189	9	-9	1	2	625	616	11	0	6	2	965	977	11
12	6	0	247	240	8	-11	3	1	43	82	43	4	8	1	209	212	10	-7	1	2	103	31	16	2	6	2	459	453	6
14	6	0	119	121	15	-9	3	1	381	388	6	6	8	1	197	200	10	-5	1	2	800	792	6	4	6	2	55	74	36
1	7	0	184	178	18	-7	3	1	1194	1199	12	8	8	1	39	64	38	-3	1	2	115	114	7	6	6	2	794	779	7
3	7	0	512	511	7	-5	3	1	1017	1024	8	10	8	1	360	354	9	-1	1	2	976	1012	6	8	6	2	514	492	6
5	7	0	329	324	7	-3	3	1	834	831	6	12	8	1	286	290	10	1	1	2	403	388	3	10	6	2	369	363	6
7	7	0	432	414	10	-1	3	1	255	236	6	14	8	1	131	142	19	3	1	2	950	949	8	12	6	2	60	46	59
9	7	0	116	109	18	1	3	1	128	138	16	-13	9	1	78	8	34	5	1	2	392	353	4	14	6	2	0	12	1
11	7	0	108	102	24	3	3	1	1390	1361	11	-11	9	1	93	87	24	7	1	2	371	358	5	-15	7	2	121	128	16
13	7	0	0	24	1	5	3	1	1987	1951	12	-9	9	1	88	52	25	9	1	2	307	288	6	-13	7	2	0	56	1
15	7	0	155	133	25	7	3	1	852	859	6	-7	9	1	253	229	10	11	1	2	53	38	52	-11	7	2	147	145	14
0	8	0	621	597	9	9	3	1	96	87	13	-5	9	1	572	588	8	13	1	2	45	94	44	-9	7	2	398	379	7
2	8	0	227	229	11	11	3	1	321	311	8	-3	9	1	148	147	14	15	1	2	100	4	26	-7	7	2	753	772	9
4	8	0	0	17	1	13	3	1	369	362	7	-1	9	1	107	110	18	17	1	2	72	70	45	-5	7	2	636	633	6
6	8	0	62	73	36	15	3	1	284	280	9	1	9	1	433	428	7	-16	2	2	156	141	22	-3	7	2	64	50	31
8	8	0	81	57	31	17	3	1	175	155	14	3	9	1	378	362	8	-14	2	2	173	136	13	-1	7	2	828	835	7
10	8	0	267	283	9	-16	4	1	61	35	61	5	9	1	254	276	15	-12	2	2	459	466	7	1	7	2	773	791	13
12	8	0	205	198	12	-14	4	1	111	101	20	7	9	1	90	39	22	-10	2	2	621	613	6	3	7	2	278	270	9
14	8	0	104	81	23	-12	4	1	298	296	8	9	9	1	87	51	22	-8	2	2	468	462	5	5	7	2	338	327	6
1	9	0	549	550	7	-10	4	1	354	348	7	11	9	1	28	77	28	-6	2	2	420	403	5	7	7	2	103	117	21
3	9	0	656	674	7	-8	4	1	360	329	7	13	9	1	135	143	18	-4	2	2	235	240	6	9	7	2	81	35	40
5	9	0	179	162	11	-6	4	1	538	505	5	-12	10	1	328	328	9	-2	2	2	808	827	9	11	7	2	76	91	27
7	9	0	161	170	12	-4	4	1	207	223	5	-10	10	1	252	256	10	0	2	2	2551	2496	17	13	7	2	200	200	9
9	9	0	427	436	7	-2	4	1	698	681	6	-8	10	1	0	51	1	2	2	2	2181	2172	15	15	7	2	188	184	11
11	9	0	57	3	56	0	4	1	974	947	8	-6	10	1	46	61	45	4	2	2	142	131	6	-14	8	2	69	91	45
13	9	0	178	182	14	2	4	1	127	135	9	-4	10	1	392	393	7	6	2	2	1143	1194	9	-12	8	2	307	302	9
0	10	0	320	338	15	4	4	1	90	84	15	-2	10	1	288	284	9	8	2	2	754	785	6	-10	8	2	207	210	11
2	10	0	93	100	32	6	4	1	132	131	10	0	10	1	552	553	7	10	2	2	872	878	8	-8	8	2	98	8	25
4	10	0	0	28	1	8	4	1	174	178	7	2	10	1	179	158	12	12	2	2	498	490	6	-6	8	2	37	22	37
6	10	0	119	107	28	10	4	1	553	556	6	4	10	1	228	231	9	14	2	2	69	72	48	-4	8	2	473	451	7
8	10	0	0	46	1	12	4	1	207	220	12	6	10	1	234	245	14	16	2	2	304	304	9	-2	8	2	740	744	15
0	8	2	362	355	7	-10	2	3	116	131	15	5	7	3	711	710	7	2	0	4	1426	1424	15	11	5	4	405	408	6
2	8	2	158	153	12	-8	2	3	209	227	11	7	7	3	73	64	30	4	0	4	287	324	6	13	5	4	205	188	9
4	8	2	196	207	10	-6	2	3	255	230	5	9	7	3	114	104	24	6	0	4	650	665	8	15	5	4	84	18	25
6	8	2	144	128	12	-4	2	3	178	184	5	11	7	3	314	323	7	8	0	4	1115	1061	13	-14	6	4	177	184	12
8	8	2	274	273	12	-2	2	3	1032	1028	6	13	7	3	174	142	13	10	0	4	698	710	9	-12	6	4	335	334	9
10	8	2	191	203	11	0	2	3	439	432	3	15	7	3	161	161	35	12	0	4	27	97	26	-10	6	4	121	126	13
12	8	2	87	37	27	2	2	3	641	661	4	-14	8	3	128	125	16	14	0	4	116	130	23	-8	6	4	272	286	8
14	8	2	63	32	57	4	2	3	568	578	4	-12	8	3	420	429	8	16	0	4	316	337	12	-6	6	4	206	180	10
-13	9	2	48	79	47	6	2	3	424	459	4	-10	8	3	254	246	9	-17	1	4	0	27	1	-4	6	4	434	436	6
-11	9	2	183	166	12	8	2	3	341	315	5	-8	8	3	97	107	20	-15	1	4	179	185	14	-2	6	4	1038	1054	8

-9	9	2	375	361	7	10	2	3	46	14	46	-6	8	3	379	365	8	-13	1	4	88	83	22	0	6	4	784	785	7
-7	9	2	381	367	7	12	2	3	39	13	39	-4	8	3	524	521	9	-11	1	4	304	300	8	2	6	4	354	364	5
-5	9	2	525	530	7	14	2	3	62	80	61	-2	8	3	759	771	7	-9	1	4	153	163	12	4	6	4	437	432	5
-3	9	2	260	246	9	16	2	3	0	37	1	0	8	3	551	580	6	-7	1	4	63	74	25	6	6	4	643	661	5
-1	9	2	432	415	7	-15	3	3	185	130	13	2	8	3	354	341	9	-5	1	4	386	378	4	8	6	4	471	478	7
1	9	2	650	659	8	-13	3	3	153	137	27	4	8	3	187	195	10	-3	1	4	1662	1655	11	10	6	4	230	225	8
3	9	2	338	334	14	-11	3	3	355	343	7	6	8	3	259	249	8	-1	1	4	2455	2500	12	12	6	4	0	58	1
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8	2	15	80	7	79	0	0	16	62	77	62	7	5	16	135	46	21	-1	5	17	207	216	16						
10	2	15	85	23	84	2	0	16	228	220	10	-4	6	16	181	193	21	1	5	17	235	217	29						

-E

APPENDIX B

Observed and calculated structure factors for 6

h	k	l	10Fo	10Fc	10s
1	0	0	950	965	12
2	0	0	558	583	9
3	0	0	428	425	5
4	0	0	354	358	5
5	0	0	916	953	10
6	0	0	1201	1253	16
7	0	0	529	532	8
8	0	0	193	192	10
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9	1	0	156	151	8
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11	1	0	83	81	15
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6	2	0	165	167	6
7	2	0	219	208	5
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9	2	0	254	260	6
10	2	0	250	242	7
11	2	0	104	111	12
12	2	0	50	39	50
13	2	0	30	41	29
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7	4	0	141	147	6
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3	9	0	198	189	8
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-6	1	1	208	218	4
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h	k	l	10Fo	10Fc	10s
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h	k	l	10Fo	10Fc	10s
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-9	3	18	94	41	25	-4	5	18	53	91	53	-1	2	19	0	16	1	-5	0	20	110	123	26	-7	3	20	56	52	55
-8	3	18	73	103	42	-3	5	18	61	52	61	0	2	19	0	16	1	-4	0	20	89	25	47	-6	3	20	67	8	43
-7	3	18	0	79	1	-2	5	18	70	24	69	1	2	19	28	98	27	-3	0	20	95	59	68	-5	3	20	85	3	32
-6	3	18	75	59	36	-1	5	18	33	48	32	2	2	19	89	85	37	-2	0	20	51	24	50	-4	3	20	46	28	45
-5	3	18	71	69	71	0	5	18	79	56	44	-8	3	19	57	65	57	-1	0	20	0	5	1	-3	3	20	91	42	22
-4	3	18	77	76	19	-10	1	19	24	47	24	-7	3	19	102	106	21	0	0	20	47	72	47	-2	3	20	145	110	12
-3	3	18	0	44	1	-9	1	19	102	89	15	-6	3	19	0	82	1	1	0	20	78	93	78	-1	3	20	82	70	18
-2	3	18	53	73	53	-8	1	19	50	51	50	-5	3	19	0	13	1	-8	1	20	88	61	23	-6	1	21	82	78	20
-1	3	18	75	93	67	-7	1	19	0	13	1	-4	3	19	77	55	45	-7	1	20	0	30	1	-5	1	21	121	116	18
0	3	18	111	65	15	-6	1	19	88	35	21	-3	3	19	0	34	1	-6	1	20	29	52	29	-4	1	21	96	84	18
1	3	18	37	29	36	-5	1	19	135	113	11	-2	3	19	130	120	12	-5	1	20	105	90	15	-3	1	21	27	32	27
2	3	18	34	19	33	-4	1	19	83	63	23	-1	3	19	117	92	14	-4	1	20	0	29	1	-2	1	21	31	7	30
3	3	18	38	23	38	-3	1	19	40	36	40	0	3	19	9	15	9	-3	1	20	69	12	25	-5	2	21	0	78	1
-8	4	18	53	41	52	-2	1	19	0	42	1	1	3	19	19	29	18	-2	1	20	39	28	39	-4	2	21	62	51	29
-7	4	18	0	3	1	-1	1	19	49	11	49	-7	4	19	102	121	23	-1	1	20	71	29	71	-3	2	21	7	7	7
-6	4	18	64	7	64	0	1	19	80	34	22	-6	4	19	113	56	21	0	1	20	0	30	1						
-5	4	18	47	55	47	1	1	19	106	131	33	-5	4	19	0	9	1	1	1	20	58	41	57						

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REFERENCES

1.Richter-Addo, G.B.; Legzdins, P. Metal Nitrosyls, Oxford University Press, New York, **1992**, pgs. 336-337.

2.Tokiwa, H.; Nakagawa, R.; Horikawa, K.; Ohkubo, A. *Environ. Health Perspect.* **1987**, *73*, 191.

3.Feldman, P.L.; Griffith, O.W.; Stuehr, D.J. *C&En* **1993**, 23.

4.Koshland, O.E., jr. *Science* **1992**, *258*, 1861.

5.Clarke, M.J.; Gaul, J.B. *Structure and Bonding.* **1993**, *81*, 147.

6.Doyle, M.O.; Hoekstra, J.W. *J.Inorg.Biochem.* **1981**, *14*, 351.

7.Lancaster, Jr, J.R., Hibbs, Jr, J.B., *Proc.Natl.Acad.Sci. USA.*, **1990**, *87*, 1223-1227.

8.Richter-Addo, G.B.; Legzdins, P. Metal Nitrosyls, Oxford University Press, New York, **1992**, pgs. 17-18.

9.Jezowska-Tresebiatowska, B.; Jezierski, A. *J.Mol.Struc.* **1973**, *19*, 635.

10.Enemark, J.H.; Feltham, R.D. *Coord.Chem.Rev.* **1974**, *13*, 339.

11.Chisholm, M.H.; Cotton, F.A.; Extine, M.W.; Kelly, R.L. *Inorg.Chem.* **1979**, *18*, 116.

12.Richter-Addo, G.B.; Legzdins, P. Metal Nitrosyls, Oxford University Press, New York, **1992**, pgs 33-68.

13.Legzdins, P.; Malito, J.T. *Inorg.Chem.* **1975**, *14*, 1875.

14.Mason, J.; Mingos, D.M.P.; Sherman, D.; Wardle, R.W. *J.Chem.Soc., Chem.Comm.* **1984**, 1223.

15.Schoonover, M.W.; Baker, E.C.; Eisenberg, R. *J.Am.Chem.Soc.* **1979**, *101*, 1880.

16.Enemark, J.H.; Feltham, R.D.; Riker-Nappier, J.; Bizot, K.F. *Inorg.Chem.* **1975**, *14*, 624.

17.Crease, A.E.; Legzdins, P.J. *J.Chem.Soc., Dalton Trans.* **1973**, 1501.

18.Legzdins, P.; Rettig, S.J.; Sanchez, L. *Organometallics* **1988**, *7*, 2394.

19.Fjare, D.E.; Gladfelter, W.L. *J.Am.Chem.Soc.* **1984**, *106*, 4799.

20.La Monica, G.; Freni, M.; Cenini, S. *J.Organomet.Chem.* **1974**, *71*, 57.

21.Fenske, R.F.; Millet, M.C. *Organometallics* **1986**, *5*, 1243.

22.Johnson, B.F.G.; Bhaduri, S.; Connelly, N.G. *J.Organomet.Chem.* **1972**, *40*, C36.

23.Mond, R.L.; Wallis, A.E. *J.Chem.Soc.* **1922**, *121*, 32.

24.Seel,F. *Z.Anorg.Allgem.Chem.* **1952**, *269*, 40.

25.Summerville, R.H.; Hoffman, R. *J.Am.Chem.Soc.* **1976**, *98*, 7240.

26.Bryar, T. McMaster University Ph.D. thesis.

27.Morris, D.E.; Basolo, F. *J.Am.Chem.Soc.* **1968**, *90*, 2531.

28.Allano, V.G.; Araneo, A.; Bellon, P.L.; Ciani, G.; Manassero, M. *J.Organomet.Chem.* **1974**, *67*, 413.

29.Hörsken, A; Zheng, G.; Stradiotto, M.; McCrory, C.T.C.; Li, L. *J.Organomet.Chem.* **1998**, *558*, 1.

30.Amoroso, D.; McCrory, C.T.C.; Zheng, G.; Li, L. unpublished results.

31.Basolo, F. *Polyhedron* **1990**, *9*, 1503.

32.Connelly, N.G. *Inorg.Chim.Acta. Reviews.* **1972**, 47.

33.Sun, S.; Sweigart, D.A. *Adv.Organomet.Chem.* **1996**, *40*, 171.
34.Huang, Y.; Carpenter, G.B.; Sweigart, D.A.; Chung, Y.K.; Lee, B.Y. *Organometallics* **1995**, *14*, 1423.
35.Hershenberger, J.W.; Klingler, R.J.; Kochi, J.K. *J.Am.Chem.Soc.* **1983**, *105*, 61.
36.Zielman, P.M.; Amatore, C.; Kochi, J.K. *J.Am.Chem.Soc.* **1984**, *106*, 3771.
37.Li, L.; Enright, G.D.; Preston, K.F. *Organometallics* **1994**, *13*, 4686.
38.McBride, D.W.; Stafford, S.L.; Stone, F.G.A. *Inorg.Chem.* **1962**, *1*, 386.
39.Reginato, N. 4th year Thesis project.
40.Atkinson, Black, J.ChemSoc. Dalton trans, 1996, 3491.
41.Richter-Addo, G.B.; Legzdins, P. Metal Nitrosyls, Oxford University Press, New York, **1992**, Chapter 2.
42.Martini, G.; Tiezzi, E. *Z.Naturforsch.* **1973**, *28b*, 300.
43.Jezowska-Tresebiatowska, B.; Jezierski, A. *J.Mol.Struc.* **1973**, *19*, 635.
44.Li, L.; Morton, J.R.; Preston, K.F. *Magn.Res in Chem.* **1996**, *33*, S20.
45.Martini, G.; Tiezzi, E. *Z.Naturforsch.* **1973**, *28b*, 300.
46.Richter-Addo, G.B.; Legzdins, P. Metal Nitrosyls, Oxford University Press, New York, **1992**, pg. 55.
47.Summerville, R.H.; Hoffman, R. *J.Am.Chem.Soc.* **1976**, *98*, 7240.
48.Amoroso, D.; McCrory, C.T.C; Li, L. unpublished results.
49.Allano, V.G.; Araneo, A.; Bellon, P.L.; Ciani, G.; Manassero, M. *J.Organomet.Chem.* **1974**, *67*, 413.
50.Amoroso, D.; McCrory, C.T.C; Li, L. unpublished results.
51.Van Berkel, G.J. in Electrospray Ionization Mass Spectrometry, pg 65-106, John Wiley and Sons, Inc., 1997.
52.Smith, R.W. McMaster University, McCrory, C.T.C. personal communication.
53.Gaskell, S.J.; *J.Mass.Spec.* **1997**, *32*, 677.
54.Hofmann, K. Imidazole and its Derivatives, Part 1. Interscience Publisher, Inc. New York, 1953, pg7-9.
55.Smith, R.W. McMaster University, McCrory, C.T.C. personal communication.
56.Jarvis, J.A.J.; Wells, A.F. *Acta Cryst.* **1960**, *13*, 1027.
57.Bauman, J.E., Jr.; Wang, J.C. *Inorg.Chem.* **1964**, *3*, 368.
58.Inoue, M.; Kishita, M.; Kubo, M. *Inorg. Chem.* **1965**, *4*, 626.
59.Bauman, J.E., Jr.; Wang, J.C. *Inorg.Chem.* **1964**, *3*, 368.
60.Rettig, S.J.; Storr, A.; Summers, D.A.; Thompson, R.C.; Trotter, J. *J.Am.Chem.Soc.* **1992**, *119*, 8675.
61.Foffani, A.; Pignataro, S.; Distefano, G.; Innorta, G.*J.Organomet.Chem.* **1967**, *7*, 473.
62.Seel, F. *Z.Anorg.Allg.Chem.* **1952**, *269*, 40.
63.Burford, N.; Muller, J.; Parks, T.M. *J.Chem.Ed.* **1994**, *9*, 807.
64.Doyle, M.P.; van Doornik, J.V.; Fundkes, C.L. *Inorg.Chim.Acta.* **1980**, *46*, L111.
65.Doyle, M..P.; Pickering, R.A.; Cook, B.R. *J.Inorg.Biochem.* **1983**, *19*, 329.
66.Mu, X.H.; Kadish, K.M. *Inorg.Chem.* **1990**, *29*, 1031.
67.Kadish, K.M.; Mu, X.H.; Lin, X.Q. *Inorg.Chem.* **1988**, *27*, 1489.