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Synthesis, characterization, and fiber-optic infrared reflectance spectroelectrochemical studies of some dinitrosyl iron diphosphine complexes $Fe(NO)_2L_2$ ($L = P(C_6H_4X)_3$)

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ABSTRACT

A series of iron dinitrosyl complexes of the form $Fe(NO)_2(P(C_6H_4X)_3)_2$ ($X = p$-OMe (**1**), p-Me (**2**), m-Me (**3**), p-H (**4**), p-F (**5**), p-Cl (**6**), p-CF_3 (**7**)) has been prepared from the reactions of $Fe(NO)_2(CO)_2$ and the respective triarylphosphines. Complexes **1**–**7** have been characterized by IR and ^{31}P NMR spectroscopy, and by X-ray crystallography for **1** and **7**. In general, the compounds with the more basic phosphines display lower ν_{NO} stretches in the IR spectra than those with the less basic phosphines, and the trends in ν_{NO} as a function of Hammett parameter and solvent donor/acceptor number were analyzed. The redox behavior of compounds **1**–**7** in CH_2Cl_2 were studied by cyclic voltammetry at a Pt electrode. In general, the compounds undergo one-electron oxidations. Infrared spectroelectrochemistry revealed that the oxidations generate the derivatives with ν_{NO}s that are ~100 cm^{-1} higher in energy indicative of $Fe(NO)_2$-centered oxidations.

1. Introduction

Iron is a major target for nitric oxide (NO) in biological systems and in the environment. The resulting ground-state Fe—N—O moiety may be linear or bent [1]. The dinitrosyl $Fe(NO)_2$ moiety has been suggested as a biologically relevant entity [2–7]. Exogenous and endogenous NO, upon exposure to and contact with Fe-containing biomolecules, generates a species exhibiting a strong EPR signal at $g = 2.03$ attributed to an "$Fe(NO)_2$"-containing species [3]. Other ligands (L) coordinate to the $Fe(NO)_2$ unit to give $Fe(NO)_2L_x$ derivatives [1]; these latter species are collectively referred to as "dinitrosyl iron compounds" (DNICs). DNICs, although mostly discussed in the literature in the realm of biology, also have significance in catalysis as mentioned below. Their syntheses and characterization, to a large extent, preceded their discovery in biology.

Synthetic DNICs display a variety of chemical properties including the ability to transfer oxygen atoms from molecular oxygen to phosphines or alkenes [8–17]. For example, Postel and co-workers demonstrated that the dinitrosyl compounds $[Fe(NO)_2X]_2$ (X = Cl, I) react with oxygen in the presence of PPh_3 or $OPPh_3$ to produce nitrato complexes such as $Fe(NO_3)_2X(OPPh_3)_2$ [8–12]. These latter nitrato complexes transfer oxygen atoms to phosphines or cyclohexene and regenerate the nitrosyl moiety [10,12].

In 1965, Maxfield reported in a patent the use of dinitrosyl iron halides as effective catalysts for the dimerization of diolefins in the presence of reducing agents [17]. Others later demonstrated that some synthetic DNICs could be used for the cyclodimerization of diolefins when reduced electrochemically [15]. Candlin [13] reported the dimerization of butadiene and isoprene by $Fe(NO)_2(CO)_2$, and Gadd [14] proposed that the photocatalytic dimerization might occur via $Fe(NO)_2(\eta^2\text{-}C_4H_6)(\eta^4\text{-}C_4H_6)$ as an intermediate. In 1994, Li [18] reported $Fe(NO)_2PPh_3(\eta^2\text{-TCNE})$ as the first stable compound containing an olefin π-bonded to an iron dinitrosyl group.

Returning to the biological significance of DNICs, it was originally proposed that DNICs formed from the reaction of NO with the active center of iron sulfur proteins [19–21]. In 2005, Ricci and co-workers reported the crystal structure of a stable complex of human glutathione transferase P1-1 containing a post-translationally modified dinitrosyl iron glutathionyl moiety [22]. It is now generally accepted that the iron in biological $Fe(NO)_2$ DNICs comes predominately from "freely chelatable iron storage units" and not necessarily from FeS proteins [23–25]. For example, Lancaster et al. recently published work describing the direct reaction of NO with the intercellular

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labile iron and found that NO rapidly and quantitatively reacts with the iron to form stable DNICs detectable by EPR [24].

All DNICs derive their basic functionality from the dinitrosyl $Fe(NO)_2$ moiety. It is known that the carbonyl ligands of $Fe(NO)_2(CO)_2$ can be replaced with σ donor ligands (L, L′) to yield dinitrosyl complexes of the form $Fe(NO)_2L_2$ or $Fe(NO)_2L'L$ [1,26,27]. Although many such complexes are known, it is somewhat surprising that only a handful of mono-phosphine $Fe(NO)_2(CO)$(-phosphine) [26–29] and diphosphine $Fe(NO)_2$(phosphine)$_2$ [8,26,29–35] compounds have been reported. In order to determine how the spectroscopic and electrochemical properties of the $Fe(NO)_2$ group are affected by small changes on the periphery of some diphosphine complexes, we have prepared and characterized a homologous series of $Fe(NO)_2(PAr_3)_2$ complexes (Ar = aryl group; allowing for a systematic variation in Ar) by FTIR and ^{31}P NMR spectroscopy, X-ray crystallography, cyclic voltammetry and fiber-optic IR spectroelectrochemistry.

2. Experimental

2.1. General

All reactions were performed under an atmosphere of prepurified nitrogen using standard Schlenk glassware and/or in a Labmaster 100 inert atmosphere glove box (Innovative Technology, Inc. Newburyport, MA). Unless otherwise indicated, all experiments were carried out at ambient room temperature.

2.2. Chemicals

Solvents were distilled under nitrogen from appropriate drying agents (CaH_2 or Na) or collected under nitrogen from a Pure Solv 400-5-MD Solvent Purification System (Innovative Technology). $Fe(NO)_2(CO)_2$ was prepared using a published method developed by Hieber and Beutner, as described by King [36]. Tris(*p*-methoxyphenyl) phosphine (98%), tri-*p*-tolylphosphine (98%), tri-*m*-tolylphosphine (98%), tri(*p*-chlorophenyl)phosphine (99%), and tris(*p*-fluorophenyl) phosphine (99%), were purchased from Strem Chemical Company (Newburyport, MA). Iron pentacarbonyl, triphenylphosphine (99%), tris(*p*-trifluoromethylphenyl)phosphine (97%) and tetrabutylammonium hexafluorophosphate (98%) were purchased from Sigma–Aldrich Chemical Company (Milwaukee, WI). Chloroform-*d* (99.8%) was purchased from Cambridge Isotope Laboratories (Andover, MA) in single-use ampoules and used as received or drawn from a stock reagent bottle and subjected to at least three freeze-pump-thaw cycles and stored over Grade 514 Type 4A molecular sieves.

2.3. Instrumentation

Infrared spectra were recorded using a Bio-Rad FTS 155 FT-IR spectrometer. $^{31}P\{^1H\}$ NMR spectra were recorded using a Varian Mercury-VX 300 MHz spectrometer equipped with a four-nuclei autoswitchable pulsed field gradient probe. All chemical shifts (δ, ppm) are reported relative to 85% H_3PO_4 as an external reference standard ($\delta = 0$ ppm).

Cyclic voltammograms were recorded using a BAS CV-50W Voltammetric Analyzer (Bioanalytical Systems, West Lafayette, IN) equipped with a three-electrode cell (3 mm Pt disk working electrode, Pt wire auxiliary electrode and a Ag/AgCl or Ag wire quasi-reference electrode). Solutions were 1 mM in analyte and 0.1 M in $[NBu_4][PF_6]$ in CH_2Cl_2. Ferrocene ($(\eta^5\text{-}C_5H_5)_2Fe$; Fc) or decamethylferrocene ($(\eta^5\text{-}C_5Me_5)_2Fe$) (Fc*; $E^{\circ\prime} = -0.55$ V vs. Fc/Fc$^+$) were used as internal reference standards. All potentials (V) are reported relative to the Fc/Fc$^+$ couple.

IR spectroelectrochemical measurements were recorded using a Bruker Vector 22 FT-IR spectrometer equipped with a Remspec mid-IR fiber-optic dip probe and a liquid nitrogen cooled MCT detector (Remspec Corporation, Charlton City, MA). The stainless steel mirror on the liquid transmission head of the fiber-optic dip probe was replaced with a 3 mm Pt disk working electrode and equipped with a custom-made electrochemical cell including a Pt wire auxiliary electrode and a Ag/AgCl or Ag wire quasi-reference electrode as described previously [37].

2.4. Synthesis

Each of the dinitrosyl iron diphosphine complexes was prepared using a method based on slightly modified literature procedures [33,38]. To the best of our knowledge, only $Fe(NO)_2(PPh_3)_2$ (compound **4**) [34,35,38] from this series was reported prior to our entry in this area. The reactions can be readily monitored by IR spectroscopy and/or ^{31}P NMR spectroscopy. For example, the reactions were considered complete when the ^{31}P NMR spectra indicated the generation of a single ^{31}P NMR peak assigned to the desired products. At the conclusion of each preparative reaction, the complexes were isolated by solvent removal *in vacuo* and purified by dissolution in CH_2Cl_2 or $CHCl_3$ followed by filtration through Celite®. Small amounts of pentane or hexane were added to the filtrates, and the products were allowed to crystallize by slow solvent evaporation under nitrogen.

2.4.1. $Fe(NO)_2(P(C_6H_4\text{-}p\text{-}OCH_3)_3)_2$ (**1**)

Dark red $Fe(NO)_2(CO)_2$ (20 μL, 0.18 mmol) was added by syringe to a toluene solution (5 mL) of $P(C_6H_4\text{-}p\text{-}OCH_3)_3$ (0.129 g, 0.37 mmol) in a Schlenk tube. The light red solution was stirred, heated and allowed to reflux under nitrogen over a period of 3 h. The solution changed from light red to black/dark brown within the first 20 min. The reaction was monitored by IR spectroscopy and stopped when the IR spectrum indicated the absence of characteristic carbonyl stretching frequencies for $Fe(NO)_2(CO)_2$ ($\nu_{CO} = 2090$ cm^{-1} and 2040 cm^{-1}) and for the expected mono-carbonyl species ($\nu_{CO} = 2002$ cm^{-1}). Isolated yield: 27%. IR (toluene, cm^{-1}): $\nu_{NO} = 1711$ s and 1667 s; also 1306 w, 1287 s, 1255 s, 1184 w, 1097 w, 826 w, 798 w. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 56.4 (s).

The other complexes were prepared similarly.

2.4.2. $Fe(NO)_2(P(C_6H_4\text{-}p\text{-}CH_3)_3)_2$ (**2**)

Reaction time = 3 h. Isolated yield: 31%. IR (toluene, cm^{-1}): $\nu_{NO} = 1714$ s and 1670 s; also 1197 w, 1189 w, 1116 w, 1095 w, 806 s $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 58.4 (s).

2.4.3. $Fe(NO)_2(P(C_6H_4\text{-}m\text{-}CH_3)_3)_2$ (**3**)

Reaction time = 5 h. Isolated yield: 23%. IR (toluene, cm^{-1}): $\nu_{NO} = 1715$ s and 1671 s; also 779 m, 588 w, 549 w. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 60.9 (s).

2.4.4. $Fe(NO)_2(PPh_3)_2$ (**4**)

The known $Fe(NO)_2(PPh_3)_2$ was prepared using a modified literature method [38]. A toluene solution (5 mL) of $P(C_6H_5)_3$ (94 mg, 0.36 mmol) was treated with $Fe(NO)_2(CO)_2$ (20 μL, 0.18 mmol) under nitrogen. The mixture was heated and allowed to reflux over a period of ~3 h. The reaction was monitored by IR spectroscopy and stopped once $Fe(NO)_2(CO)_2$ ($\nu_{CO} = 2090$ cm^{-1} and 2040 cm^{-1}) or the known $Fe(NO)_2(PPh_3)(CO)$ ($\nu_{CO} = 2005$ cm^{-1}) were no longer detected. Isolated yield: 22%. IR (toluene, cm^{-1}): $\nu_{NO} = 1719$ s and 1678 s; also 1203 m, 1119 m, 543 m. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 60.9 (s).