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Di-Iron Aza Diphosphido Complexes: Mimics for the Active Site of Fe-Only Hydrogenase, and Effects of Changing the Coordinating Atoms of the Bridging Ligand in $[Fe_2\{\mu\text{-}(ECH_2)_2NR\}(CO)_6]$

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The bis(phosphido)-bridged complex $[Fe_2(\mu\text{-}PPhH)_2(CO)_6]$ (**1**) undergoes double deprotonation to give the phosphorus-centered dianionic derivative $[Fe_2(\mu\text{-}PPh)_2(CO)_6]^{2-}$ (**2**) which in turn reacts with the tertiary base $RN(CH_2Cl)_2$ to give $[Fe_2\{(PPhCH_2)_2NR\}(CO)_6]$ (**3**) in moderate yield. Treatment of **3** with $HBF_4{\cdot}Et_2O$ affords the N-protonated species $[Fe_2\{(PPhCH_2)_2NHR\}(CO)_6]\ BF_4$ (**4**). The structural changes to the heavy atom skeleton of **3** arising from protonation are slight, the most obvious being a ca. 0.03 Å lengthening of the N–C bonds.

Attempts to model the di-iron subsite of all-iron hydrogenase have led to a significant renaissance in the chemistry of sulfur-rich di-iron carbonyls. For example, interest has recently been focused on such bimetallic species as $[Fe_2(\mu\text{-}S_2C_3H_6)(CO)_6]$, $[Fe_2\{\mu\text{-}(SCH_2)_2CMeSR\}(CO)_5]$, and $[Fe_2\{\mu\text{-}(SCH_2)_2NR\}(CO)_6]$.[1] In particular, cyanation of these penta- and hexa-carbonyl systems and protonation of some of their derivatives have both been reported. These efforts have so far been unsuccessful in elucidating the mechanisms of hydrogen production and uptake.[2] Moreover, till now none of the complexes proposed as a chemical model for the enzyme has shown high efficiency in hydrogen production.[3]

Very recently, we have been interested in the electrochemical behavior of the di-iron hexacarbonyl aza-dithiolate complex $[Fe_2\{\mu\text{-}(SCH_2)_2NCH_2CH_2OMe\}(CO)_6]$ in the presence of acid.[4] The effects of changing the coordinating atoms of the bridging ligand on the activity of such a complex have not so far been investigated. This has prompted us to substitute the sulfur atoms in $[Fe_2\{\mu\text{-}(SCH_2)_2NR\}(CO)_6]$ species with {RP} units in the hope of obtaining new insight into the chemistry of models of the enzymatic di-iron subsite and a better understanding of their electrochemistry. Although some μ-diphosphido complexes $[Fe_2(\mu\text{-}PhP{-}R{-}PPh)(CO)_6]$ containing various organic bridges between the two phosphorus atoms have been reported, to the best of our knowledge no di-iron aza-diphosphido complexes of general formula $[Fe_2\{(PRCH_2)_2NR\}(CO)_6]$ have previously been prepared.[5,6] Widely applicable synthetic routes to the new class of polydentate N-functionalized 2-aza-1,3-dithiolate ligands $RN(CH_2S)_2^{2-}$ have recently become available; they are based on the di-iron precursors $[Fe_2(\mu\text{-}SH)_2(CO)_6]$ and $[Fe_2(\mu\text{-}S)_2(CO)_6]^{2-}$.[3e,7,8] Several years ago, it was reported that a phosphorus analogue of $[Fe_2(\mu\text{-}SH)_2(CO)_6]$, namely the bis(phosphido) complex $[Fe_2(\mu\text{-}PPhH)_2(CO)_6]$ (**1**), could be deprotonated with MeLi or Et_3N to give the phosphorus-

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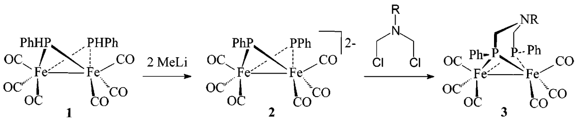
Scheme 1



centered dianion $[Fe_2(\mu\text{-}PPh)_2(CO)_6]^{2-}$ (**2**). This in turn can react, like $[Fe_2(\mu\text{-}S)_2(CO)_6]^{2-}$, with various organic di-halides (X−R−X) to give the complexes $[Fe_2(\mu\text{-}PhP{-}R{-}PPh)(CO)_6]$ (R = C_2H_4, C_3H_6, $CH_2C_6H_4CH_2$).[5,6k,9] These complexes were, however, obtained in only moderate yield, probably because of a competing reaction which gives bis(phosphido)-bridged complexes $[Fe_2(\mu\text{-}PhP{-}RX)_2(CO)_6]$ containing haloalkyl groups. We are now extending the use of the deprotonation reaction of $[Fe_2(\mu\text{-}PPhH)_2(CO)_6]$ (**1**) as a general synthetic route to new di-iron aza-diphosphido complexes. The appearance during the course of our writing of a paper devoted to the electrocatalytic reduction of the phosphido-bridged di-iron compounds $[Fe_2(\mu\text{-}PPh_2)_2(CO)_6]$[10] in the presence of protons prompts us to report our preliminary results on the formation of $[Fe_2\{(P(Ph)CH_2)_2NR\}(CO)_6]$ (**3**) and its subsequent protonation.

Treatment of $Li_2[Fe_2(\mu\text{-}PPh_2)_2(CO)_6]$ with $(ClCH_2)_2NCH_2CH_2OMe$ afforded $[Fe_2\{(PPhCH_2)_2NCH_2CH_2OMe\}(CO)_6]$ (**3**) as yellow crystals in 41% yield (Scheme 1).[11]

Compound **3** was characterized by elemental analyses and IR and NMR spectroscopy. Typical strong bands at 2054, 2015, 1985, and 1971 cm^{-1} are observed in the carbonyl region of the infrared spectrum of CH_2Cl_2 solutions of **3**.[5,6,12] The ν(CO) absorptions are shifted to lower frequencies relative to those of the thiolato analogue $[Fe_2\{\mu\text{-}(SCH_2)_2NCH_2CH_2OMe\}(CO)_6]$ (ν(CO) = 2073, 2034, 1994 cm^{-1})[4] suggesting that the $(PPhCH_2)_2NR$ di-phosphido bridge has a greater ability to donate electrons than the $(SCH_2)_2NR$ μ-dithiolato unit. The ^1H NMR spectrum of **3** displays the set of resonances expected for the $(PPhCH_2)_2NCH_2CH_2OMe$ group.[4] Its $^{31}P\{^1H\}$ NMR spectrum shows a single resonance, indicating that the two phosphido bridges are equivalent; moreover, the chemical shift of 134.4 ppm is consistent with the presence of an Fe−Fe bond.[13] The structure of **3** was confirmed by X-ray analysis of a single crystal obtained from hexane−dichloromethane solution (Figure 1).[14] This establishes that **3** contains a bidentate aza-diphosphido group $(PPhCH_2)_2NCH_2CH_2OMe$ which uses both its phophorus atoms to bridge the iron atoms of a $\{Fe_2(CO)_6\}$ core. It is structurally closely analogous to other known di-iron(I) hexacarbonyl complexes containing two phosphido bridges in which the $\{Fe_2P_2\}$ core adopts a butterfly conformation.[5a,6j,12a,15] Two eclipsed $Fe(CO)_3$ units are linked by a direct Fe−Fe bond in addition to being bridged by the diphosphido group. The Fe−Fe bond length [2.631(1) Å] is typical of the values found in other dimeric Fe(I) complexes $[Fe_2(\mu\text{-}PhP{-}R{-}PPh)(CO)_6]$ (R = C_3H_6, $CH_2C_6H_4CH_2$)[5a,6j] or $[Fe_2(\mu\text{-}PR_2)(\mu\text{-}PR'_2)(CO)_6]$[12a,15] but is longer by 0.12 Å than the corresponding bond in the aza-dithiolato-bridged species $[Fe_2\{\mu\text{-}(SCH_2)_2NCH_2CH_2OMe\}(CO)_6]$.[4] The resulting coordination geometry around each Fe atom can be described as a distorted square-pyramid supplemented by the Fe(I)−Fe(I) single bond required by normal electron counting rules. Steric constraint enforced by the aza bridge shortens significantly the intramolecular P1···P2 contact [2.699(1) Å] relative to those observed in other phosphido complexes where there is no organic bridge between the two phosphorus

Figure 1. Structure of $[Fe_2\{(P(Ph)CH_2)_2NCH_2CH_2OCH_3\}(CO)_6]$ (**3**) showing 50% thermal ellipsoids. Selected distances (Å): Fe−Fe 2.631(1); Fe−P 2.200(1)−2.206(1); Fe−C 1.782(2)−1.809(2)’ P−Ph 1.823(2)−1.825(2); P−CH_2 1.846(2)−1.849(2); N−C 1.462(2)−1.475(2).

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(14) Crystal data for **3**: $C_{23}H_{21}Fe_2NO_7P_2$, fw = 597.05, T = 100 K, orthorhombic, space group *Pbna*, a = 7.9647(1) Å, b = 20.4402(1) Å, c = 31.0173(3) Å, V = 5049.62(8) Å^3, Z = 8. Refinement of 317 parameters gave R1 = 0.042, wR2 = 0.072, and $|\Delta\rho| < 0.46$ e·Å^{-3} for all 6077 unique reflections. For **4**: $C_{23}H_{22}BF_4Fe_2NO_7P_2$, fw = 684.87, T = 115 K, monoclinic, space group $P2_1$, a = 8.9407(3) Å, b = 30.145(1) Å, c = 11.2557(3) Å, β = 112.167(1)°, V = 2809.4(2) Å^3, Z = 4. Refinement of 731 parameters gave R1 = 0.044, wR2 = 0.071, and $|\Delta\rho| < 0.39$ e·Å^{-3} for all 12131 unique reflections. Further crystallographic data for **3** and **4** are provided as Supporting Information.

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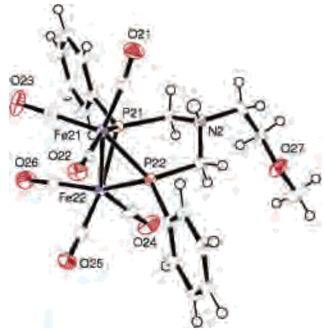
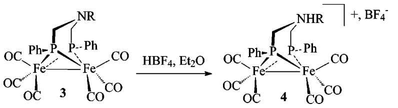


Figure 2. View of one of the two independent $[Fe_2\{(P(Ph)CH_2)_2NHCH_2CH_2OCH_3\}(CO)_6]^+$ (**4**) cations (50% ellipsoids). Selected distance (Å) and angle (deg) ranges (for both cations): Fe−Fe 2.633(1)−2.639(1); Fe−P 2.191(1)−2.215(1); Fe−C 1.780(3)−1.811(3); P−Ph 1.814(3)−1.820(3); P−CH_2 1.853(3)−1.862(3); N−C 1.490(4)−1.521(4); P···P 2.715(1)−2.721(1); C−N−C 111.9(2)−113.1(2); C−N−H 102(2)−110(2).

Scheme 2



atoms [2.725(2)−2.925(4) Å].[15a] The Fe2−P2−C8−N1−C7−P1 metalloheterocycle has a chair conformation with the N-substituent in an equatorial position. C7, C8, and C9 define a nearly ideal trigonal pyramid about N1 [C8−N1−C7 112.8(1)°, C8−N1−C9 108.4(1)°,and C7−N1−C9 111.8(1)°]. The P−CH_2 bond lengths [1.849(2) and 1.846(2) Å] are slightly shorter than those in $[Fe_2(\mu\text{-PhP}-R-\text{PPh})(CO)_6]$ ($R = CH_2C_6H_4CH_2$) [1.876(9) and 1.880(8) Å].[5a] Other distances and angles are unexceptional.

Protonation of **3** in CH_2Cl_2 with $HBF_4{\cdot}Et_2O$ afforded a yellow solution of $[Fe_2\{(PPhCH_2)_2NHCH_2CH_2OMe\}(CO)_6]BF_4$ (**4**). Addition of Et_2O precipitated **4** as a yellow powder (Scheme 2).[11]

The carbonyl absorptions in the IR spectrum of **4** are shifted ca. 19 cm^{-1} to higher energy relative to those of **3**, consistent with N-protonation.[3b,e,4,8b,c,16] The ^1H NMR spectrum of **4** also confirms that protonation does not occur at the Fe−Fe site. Instead of the characteristic high-field signal of an $Fe_2(\mu\text{-}H)$ group, a broad resonance at 6.23 ppm was detected, suggesting unambiguously that the proton involved was attached to the nitrogen atom. As previously observed for the dithiolate analogues,[3e] the resonances of protons on carbon atoms bonded to the protonated nitrogen atom are shifted to lower field compared with those of **3**. The ^{31}P NMR signal of the phosphido bridges in **4** ($\delta = 114.8$) still lies in the range typical of binuclear metal−metal bonded systems, though at higher field than the corresponding resonance for **3**. An X-ray analysis of **4** (Figure 2) confirms that protonation has occurred on the nitrogen atom of **3**.[14] Crystals of **4** contain two crystallographically independent but structurally identical (rms Δ 0.10 Å) cations. Comparison of Figure 2 with Figure 1 shows that the heavy atom skeletons of **3** and **4**, including even the CH_2CH_2OMe side chains, are barely distinguishable from one another.

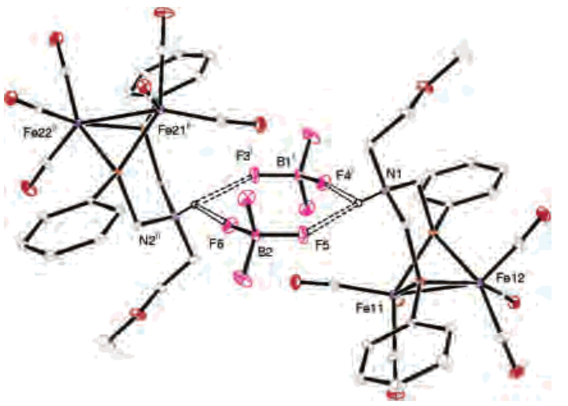


Figure 3. Asymmetric unit of **4** showing the hydrogen-bonded $[Fe_2\{(P(Ph)CH_2)_2NHCH_2CH_2OCH_3\}(CO)_6]BF_4$ dimer. Hydrogen bonds are indicated by broken lines. Phenyl and methylene H-atoms are omitted for clarity. Symmetry code: (i) $1 + x, y, z$; (ii) $2 - x, {}^1/_2 + y, -z$.

The cations of **4** again contain Fe−P−C−N−C−P rings in chair conformations with equatorial N-methoxyethyl substituents. The most obvious consequences of N-protonation are (i) opening of one Fe−Fe−C angle in each cation by ca. 10° to relieve H/CO steric crowding [e.g., compare Fe22−Fe21−CO21 153.3(1)° and Fe21−Fe22−CO24 143.4(1)°] and (ii) slight extension of the N−C bonds in **4** [1.490(4)−1.521(4) Å] compared with those in **3** [1.462(2)−1.475(2) Å]. Both N-bonded protons were located experimentally and prove to be involved in bifurcated hydrogen bonds to BF_4^- anions; indeed, the asymmetric unit is an approximately centrosymmetric dimer which contains a ring formed by N−H···F bonds which link cations and anions (Figure 3). It is worth noting that a protonated form of the thiolato analogue $[Fe_2\{\mu\text{-}(SCH_2)_2NCH_2CH_2OMe\}(CO)_6]$ cannot be isolated.[4] This seems to reflect, at least partly, an increase in steric crowding of the aza-nitrogen atom when P is replaced by S in the bridging ligand: in the thiolato species the shortest intramolecular N···Fe and N···C(carbonyl) contacts are 3.280(3) and 3.021(3) Å whereas the corresponding values in **3** are 3.531(2) and 3.168(2) Å, rising to at least 3.581(2) and 3.595(4) Å in **4**.

In this work, we show cleanly that by substituting the sulfur-bridged ligands in di-iron carbonyl compounds with aza-diphosphido ones, we identify the active site of protonation on the nitrogen atom. Moreover, it appears that our results are clearly relevant to the processes by which enzymes catalyze the reduction of protons. Further experiments on protonation of **3** are in progress, and we are also investigating cyanation of **3** and its reduction behavior in the presence of protons.

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Supporting Information Available: Synthetic, spectroscopic, and analytical data for **3** and **4**, crystallographic information file (CIF), and additional tables of crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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