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Metal carbonyl analogues of iron–sulfur clusters found in metalloenzyme chemistry

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Contents

Abstract

Many iron–sulfur metalloenzymes are based on Fe_4S_4 cubes in which the iron sites have high-spin tetrahedral coordination. Such Fe_4S_4 cubes can be obtained by dimerization of Fe_2S_2 rhombuses. Similar cluster aggregation processes can be observed for model Fe–S systems in which the high-spin tetrahedral iron sites are replaced by low-spin octahedral $Fe(CO)_3S_3$ sites. The Fe_2S_2 analogue for the metal carbonyl system is $Fe_2(CO)_6S_2$, whose ground-state structure contains a Fe_2S_2 tetrahedron with Fe–Fe and S–S bonds as well as four Fe–S bonds. However, much of the observed photochemistry of $Fe_2(CO)_6S_2$ can be rationalized by a coordinatively unsaturated rhombus photointermediate in which the Fe–Fe

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and S–S bonds of the ground state have broken in a concerted process in accordance with molecular orbital calculations. Additional insight into the chemistry of these iron carbonyl sulfides is obtained by replacement of the sulfur atoms by isoelectronic RP groups. Thus the stable $\mathrm{Fe_2(CO)_6(P^tBu)_2}$ tetrahedron and the stable rhombus $\mathrm{Fe_2(CO)_6(POC_6H_2\text{-}4\text{-}Me\text{-}2,6\text{-}{}^tBu_2)_2}$ can both be isolated and characterized. In addition, the reaction of $\mathrm{Na_2Fe(CO)_4}$ with $\mathrm{{}^iPr_2NPCl_2}$ gives the phosphorus-bridging carbonyl derivative $\mathrm{({}^iPr_2NP)_2COFe_2(CO)_6}$, which undergoes thermal reactions with unsaturated organic molecules to give adducts of their C=C, C=O, or C≡N bonds to the phosphorus atoms of a $\mathrm{Fe_2(CO)_6(PN^iPr_2)_2}$ unit generated by extrusion of the phosphorus-bridging carbonyl group. A low-temperature IR spectroscopic study of $\mathrm{({}^iPr_2NP)_2COFe_2(CO)_6}$ photolyzed in a Nujol matrix provides evidence for an unstable nearly square $\mathrm{Fe_2(CO)_6(PN^iPr_2)_2}$ rhombus. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Metal carbonyl analogues; Iron–sulfur clusters; Metalloenzyme chemistry

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1. Introduction

Iron–sulfur cluster units have been recognized since the 1970s as key building blocks for an increasing number of metalloenzymes involved in biological redox processes [1–5]. The key to this redox reactivity appears to be the $\mathrm{Fe_4S_4}$ cube (Fig. 1), which can assume a variety of redox states and thus act as an electron source or sink. Thus the $\mathrm{Fe_4S_4}$ cube has been demonstrated to play a key role in redox processes involved in the chemistry of the nitrogenase Fe–Mo–S metalloprotein [6] and the Fe-only hydrogenase from *Clostridium pasteurianum* [7].

The relationships between the most important known iron–sulfur clusters in metalloenzymes are depicted in Fig. 1. The fundamental building block is the $\mathrm{Fe_2S_2}$ rhombus [8], which can dimerize to the $\mathrm{Fe_4S_4}$ cube. One iron vertex can be removed from the $\mathrm{Fe_4S_4}$ cube to give a $\mathrm{Fe_3S_4}$ unit, which can function as a tridentate ligand

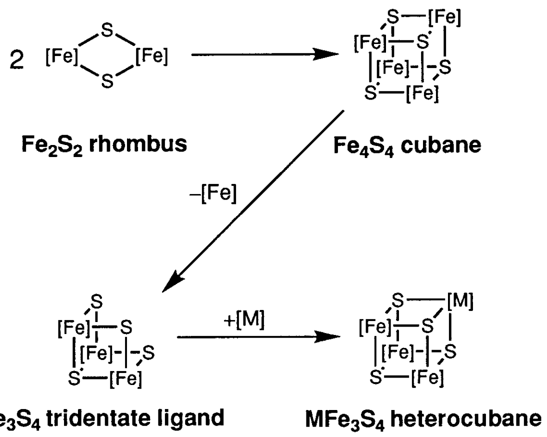

Fig. 1. Some of the important iron–sulfur cluster units found in metalloenzymes. The iron vertices, designated as [Fe], have high-spin tetrahedral $\mathrm{FeS_4}$ coordination.

towards another metal atom to give heterometallic MFe_3S_4 cubes [9] among which the molybdenum derivatives ($M = Mo$) are particularly relevant to nitrogenase chemistry. The terminal groups in these iron-cluster sulfur structures as found in vivo are thiolate groups derived from protein cysteine residues although synthetic analogues derived from a variety of less complicated abiotic thiols (e.g. benzenethiol) are also known [10]. The local iron environments in these structures are typically high-spin tetrahedral FeS_4 in the general form $(RS)_2FeS_{2/2}$ or $RSFeS_{3/3}$ depending upon the nuclearity where, e.g. $S_{2/2}$ refers to two sulfur atoms each bridging two iron atoms. Model mononuclear compounds of the general type $Fe(SR)_4^{z-}$ have been characterized for both Fe(II) ($z = 2$) and Fe(III) ($z = 1$) [11]. Because of the high-spin iron atoms in these tetrahedral FeS_4 building blocks, the magnetic interactions in the polynuclear structures are rather complicated and have been the subject of considerable experimental and theoretical studies [12]. The model iron–sulfur clusters of various nuclearities are readily synthesized from mixtures of kinetically labile Fe(II) or Fe(III) salts, sulfide, and a suitable thiol under suitable conditions with the nature of the product being influenced by the mole ratios of the reactants [10].

A question of interest is whether analogous iron–sulfur cluster structures can be obtained based on kinetically inert diamagnetic octahedral Fe(II) units rather than kinetically labile paramagnetic tetrahedral iron units. The use of kinetically inert octahedral iron structural units might allow isolation of iron–sulfur cluster structure types, which are too reactive to be isolated using kinetically labile tetrahedral iron units and thus could provide additional insight into processes for the construction of iron–sulfur clusters of various nuclearities. In addition the structure of the Fe-only hydrogenase from *C. pasteurianum* was recently found to contain a Fe_2S_2 cluster with octahedrally coordinated iron [7]. Recent Mössbauer studies indicate that this Fe_2S_2 cluster contains low spin iron and plays a key role in the redox properties of this metalloenzyme [13].

The specific approach to the modeling of Fe–S cluster metalloenzyme chemistry discussed in this paper (Fig. 2) uses octahedral iron tricarbonyl sulfur units of the

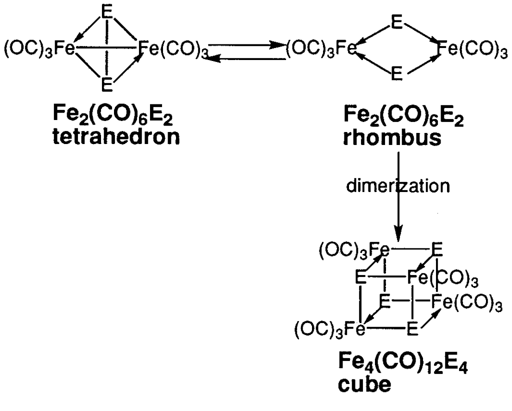

Fig. 2. Some of the important iron carbonyl chalcogen cluster units (E = S, Se, Te).

general type $Fe(CO)_3S_{3/3}$ to construct a $Fe_4(CO)_{12}S_4$ cube, which has been obtained by photochemical dimerization [14] of a $Fe_2(CO)_6S_2$ rhombus. However, the binuclear complex $Fe_2(CO)_6S_2$ is not a rhombus but instead an isomeric Fe_2S_2 tetrahedron obtained by bridging the diagonals of a Fe_2S_2 rhombus with additional Fe–Fe and S–S bonds. In addition, the substitution of the S atoms in $Fe_2(CO)_6S_2$ with RP units of various types provides a way of tuning the chemical reactivity of the Fe_2E_2 unit. Of particular significance is the use of bulky R′OP vertices to stabilize a Fe_2P_2 complex $Fe_2(CO)_6(POC_6H_2\text{-4-Me-2,6-}^tBu_2)_2$, as a rhombus rather than a tetrahedron [15].

2. Chemistry of the iron carbonyl chalcogenide clusters $Fe_2(CO)_6E_2$ (E = S, Se, Te) and related compounds

2.1. The cluster $Fe_2(CO)_6S_2$

The $Fe_2(CO)_6S_2$ cluster is a volatile red air-stable solid, m.p. 46–47°C, which was first reported by Hieber and Gruber [16] in 1958 as a product from the rather smelly reaction of $Fe(CO)_5$ with KOH and polysulfide in aqueous alcohol followed by acidification. This reaction still appears to be the only general method for the synthesis of this cluster although some improvements have been made [14,17] since the original report. Because of the relatively low costs of the starting materials required for its synthesis, the cluster $Fe_2(CO)_6S_2$ is readily available in quantities sufficient for a detailed study of its chemistry.

Determination of the structure of $Fe_2(CO)_6S_2$ by X-ray diffraction clearly indicates the presence of a Fe_2S_2 tetrahedron with a Fe–Fe bond length of 2.55 Å and a S–S bond length of 2.01 Å in addition to four Fe–S bond lengths of 2.23 ± 0.01 Å [18,19]. Hartree–Fock calculations of this structure indicate that the highest occupied molecular orbital (HOMO) is Fe–Fe bonding but that the lowest unoccupied molecular orbital (LUMO) is S–S antibonding. The nature of the HOMO has been confirmed by photoelectron spectroscopic studies [20,21].

The electronic spectrum of $Fe_2(CO)_6S_2$ in acetonitrile shows absorptions at $\lambda_{max} = 449$ ($\varepsilon = 1080$ M^{-1} cm^{-1}), 336 (11 200), 278 (8 300), and 218 nm (27 600). The longest energy band is slightly solvatochromic and has been assigned to a metal–ligand charge-transfer (MLCT) transition [22]. Photolysis of $Fe_2(CO)_6S_2$ with a variety of unsaturated molecules leads to products derived from addition reactions across the S–S bond (Fig. 3). Such photochemical reactions can be interpreted as involving a Fe_2S_2 rhombus photointermediate derived from the tetrahedrane $Fe_2(CO)_6S_2$ by breaking both the Fe–Fe and S–S bonds in the Fe_2S_2 unit (Fig. 2). Both iron atoms in this $Fe_2(CO)_6S_2$ rhombus thus are coordinatively unsaturated five-coordinate Fe(II) and are expected to be highly reactive. In this connection addition of an unsaturated molecule across the pair of sulfur atoms in the $Fe_2(CO)_6S_2$ rhombus leads to concurrent reformation of the Fe–Fe bond. Such photochemical addition reactions to $Fe_2(CO)_6S_2$ are known for ethylene [23,24], higher acyclic [25] and cyclic [26] alkenes, dienes, and trienes [24]. The ethylene adduct, $C_2H_4S_2Fe_2(CO)_6$ (Fig. 3) was already a known compound, previously

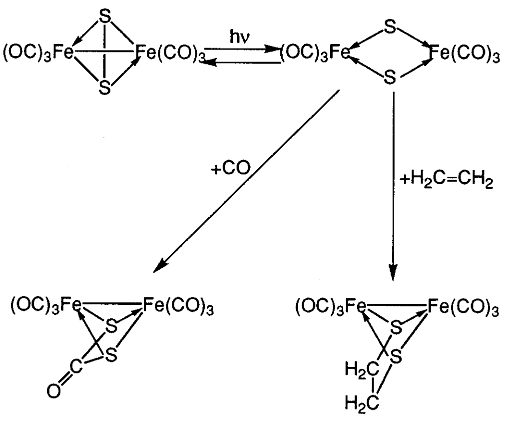

Fig. 3. Photolysis of $Fe_2(CO)_6S_2$ with CO and CH_2=CH_2.

obtained from reactions of 1,2-ethanedithiol with $Fe(CO)_5$ or $Fe_3(CO)_{12}$ [27]. Photolysis of $Fe_2(CO)_6S_2$ in the absence of a substrate to trap the $Fe_2(CO)_6S_2$ rhombus leads to its dimerization to form the $Fe_4(CO)_{12}S_4$ cube (Fig. 3), as a black air-stable crystalline solid sparingly soluble even in organic solvents [14]. This $Fe_4(CO)_{12}S_4$ cube had been previously obtained by reaction of the nitrosyl Fe_4S_4 cubane $Fe_4(NO)_4(\mu_3\text{-}S)_4$ in toluene solution with CO at 80°C/200 atm [28].

Recent photolysis studies of $Fe_2(CO)_6S_2$ in frozen Nujol at ca. 90 K have revealed that excitation into the MLCT band results in the formation of a new species without loss of CO. The spectrum of this species is consistent with a Fe_2S_2 rhombus of either D_{2h} or C_2 symmetry. Photolysis into the higher energy absorption bands of $Fe_2(CO)_6S_2$ result in loss of CO from the rhombus [29]. The Fe_2S_2 rhombus is assumed to be an intermediate in both the photodimerization and alkene addition reactions discussed above. Photochemical addition of CO to $Fe_2(CO)_6S_2$ has also been reported, but difficulties in reproducing this result have not yet allowed an assignment of the probable reaction intermediate. The carbon monoxide adduct, $S_2COFe_2(CO)_6$ (Fig. 3), can be isolated in low yield from the reaction of $Fe_3(CO)_{12}$ with sulfur [30].

Substitution of carbonyl ligands in $Fe_2(CO)_6S_2$ by phosphine and phosphite ligands has been extensively studied. Substitution of a single carbonyl by a phosphine always appears to occur at the axial position, *trans* to the Fe–Fe bond [31]. Double substitution occurs predominantly in a *trans,trans* conformation although spectral evidence indicates that traces of a second structural isomer may be formed.

Kinetic studies of the reaction of $Fe_2(CO)_6S_2$ with phosphines have yielded second-order rate laws for $L = PPh_3$, $AsPh_3$, $P(OCH_2)_3CC_2H_5$, $P(OPh)_3$, and $PPhEt_2$, while the rate law for PBu_3 appears to have both second- and third-order rate terms [32]. Reaction of $Fe_2(CO)_6S_2$ with PPh_3 has been observed to form an adduct that has the same number and pattern of carbonyl bands as the parent compound but with these bands shifted down in frequency near to those of

$Fe_2(CO)_5(PPh_3)S_2$. These data have been interpreted as implying an intermediate in which the phosphine bridges the two iron atoms. Interestingly, kinetic studies of the reaction of $Fe_3(CO)_9X_2$, where X = S or Se, with phosphines have yielded very similar results, but in this case they have been interpreted to suggest that the incoming ligand complexes initially at the chalcogen and then rearranges to transfer the ligand to the metal [33]. It is now known that the more likely site of nucleophilic attack on $Fe_2(CO)_6S_2$ is at the LUMO S–S antibond. Indeed, nucleophiles such as alkyl lithium and Grignard reagents react exclusively at the S–S bond and it seems likely that phosphines would also prefer this site. The anomalous behavior of PBu_3 may be understood as arising from the greater basicity of this reagent relative to aryl phosphines and phosphites, thus resulting in a more stable adduct that may be able to react with a second PBu_3 molecule through a mechanism similar to that of $Fe_2(CO)_6(\mu\text{-SR})_2$ reactions, vide infra. A test of this hypothesis with the highly basic PMe_3 ligand should serve to clarify this mechanism.

Reaction of $Fe_2(CO)_6S_2$ with I_2 results in the formation of an ionic product with the formula $Fe_3(CO)_6S_2I_5$. This species may be formulated as $[Fe_2(CO)_6(\mu\text{-I})S_2]FeI_4$ or $[Fe_2(CO)_6(\mu\text{-FeI}_4)S_2]I$. Reaction of I_2 with $Fe_2(CO)_4(PPh_3)_2S_2$ yields a product with a bridging iodide, while reactions with Br_2 and Cl_2 produce trinuclear products [34].

The behavior of $Fe_2(CO)_6S_2$ upon reduction is also consistent with the S–S antibonding nature of its LUMO. Thus two-electron reduction of $Fe_2(CO)_6S_2$ with sodium, KH, or $LiBHEt_3$ at −78°C in tetrahydrofuran leads to the butterfly-shaped dianion $Fe_2(CO)_6S_2^{2-}$ in which the S–S bond has been broken (Fig. 4) [17] in accordance with the two additional electrons populating the S–S antibonding orbital. An intermediate product of this reduction is the green μ-disulfide dianion $[(\mu\text{-S})Fe_2(CO)_6(\mu_4\text{-S–S})Fe_2(CO)_6(\mu\text{-S})]^{2-}$ apparently formed by dimerization of a $Fe_2(CO)_6S_2^-$ radical anion one-electron reduction product through formation of a S–S bond bridging two $Fe_2(CO)_6$ units (Fig. 4) [35]. The $Fe_2(CO)_6S_2^{2-}$ dianion is reactive towards a variety of electrophiles (Fig. 5) such as alkyl halides to give $(RS)_2Fe_2(CO)_6$ derivatives and 1,2-dibromoethane to give $C_2H_4S_2Fe_2(CO)_6$ identical to the product obtained from the photochemical addition of ethylene to $Fe_2(CO)_6S_2$ (Fig. 3) [17]. Protonation of the $Fe_2(CO)_6S_2^{2-}$ dianion with CF_3CO_2H gives the novel dithiol $Fe_2(CO)_6(SH)_2$, a dark-red air-stable solid, m.p. 74–76°C, which can be regarded as an inorganic mimic of organic thiols [36].

The dianion $Fe_2(CO)_6S_2^{2-}$ forms a variety of bidentate chelates with metals and metalloids such as Si, Ge, Sn, Ni, Pd, and Pt (Fig. 5) [17]. Some of these metal chelates can also be obtained by insertion of low valent metal species such as $(Ph_2PCH_2CH_2PPh_2)Ni^0$, $(Ph_3P)_2Pd^0$, $(Ph_3P)_2Pt^0$, $\eta^5\text{-}C_5H_5Co^I$, and $(CH_3)_2Sn^{II}$ into the S–S bond of neutral $Fe_2(CO)_6S_2$ [37]. In addition, reactions of $Fe_2(CO)_6S_2^{2-}$ with various molybdenum reagents provide an organometallic approach to a variety of Fe–Mo–S clusters with carbonyl end-groups of interest in modeling various aspects of the iron–molybdenum cofactor of nitrogenase [38]. For example reaction of two to three equivalents of $Fe_2(CO)_6S_2^{2-}$ with $[Mo(CO)_4I_3]^-$ in tetrahydrofuran was found to give [39] $[Mo\{S_2Fe_2(CO)_6\}\{S_4Fe_4(CO)_{10}\}]^{2-}$ and $[Fe_2(CO)_6SMo(CO)_2\{S_2Fe_2(CO)_6\}]^{2-}$. Similarly the reaction of one equivalent of

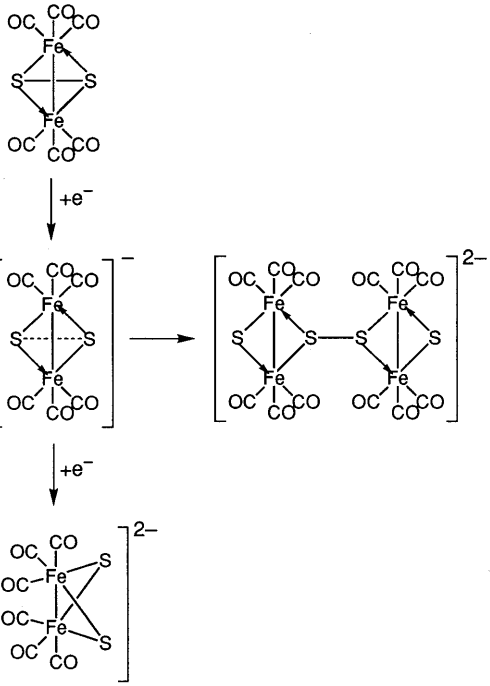

Fig. 4. Reduction of $Fe_2(CO)_6S_2$ to anionic derivatives. The reductions are typically performed using sodium, KH, and preferably $LiBHEt_3$ in tetrahydrofuran solution at −78°C.

$Fe_2(CO)_6S_2^{2-}$ with $Mo(CO)_5I^-$ gives both the same $[Fe_2(CO)_6SMo(CO)_2\{S_2Fe_2(CO)_6\}]^{2-}$ and a new cluster $[Fe_2(CO)_6S_2\{Mo(CO)_3\}_2]^{2-}$. The structures of these Fe–Mo–S clusters, which have been determined by X-ray diffraction [39], are rather complicated and exhibit relatively low symmetry. However, they can be derived from the hypothetical molybdenum chelates $[Mo\{S_2Fe_2(CO)_6\}_3]^{2-}$, $[Mo(CO)_2\{S_2Fe_2(CO)_6\}_2]^{2-}$ and $[Mo_2(CO)_6S_2Fe_2(CO)_6]^{2-}$, respectively, of the bidentate $Fe_2(CO)_6S_2^{2-}$ ligand (Fig. 5) by various combinations of decarbonylation, sulfur extrusion, and Mo–Fe bond formation.

2.2. The derivatives $Fe_2(CO)_6(\mu\text{-}SR)_2$ and $Fe_2(CO)_6(\mu\text{-}S_2Z)$ (Z = divalent organic group)

Extensive chemistry has been developed for organosulfide derivatives of $Fe_2(CO)_6S_2$ of the general formulas $Fe_2(CO)_6(\mu\text{-}SR)_2$ and $Fe_2(CO)_6(\mu\text{-}S_2Z)$ (Z = divalent organic group such as $-(CH_2)_n-$ or $o\text{-}C_6H_4$). Such compounds may be prepared by reaction of $Fe_2(CO)_9$ or $Fe(CO)_5$ with R_2S_2 or RSH, reaction of $Fe_2(CO)_6S_2^{2-}$ with RX or ZX_2, or photoaddition of $RCH{=}CH_2$ to $Fe_2(CO)_6S_2$. X-ray structures of these compounds confirm that the tetrahedrane geometry of the

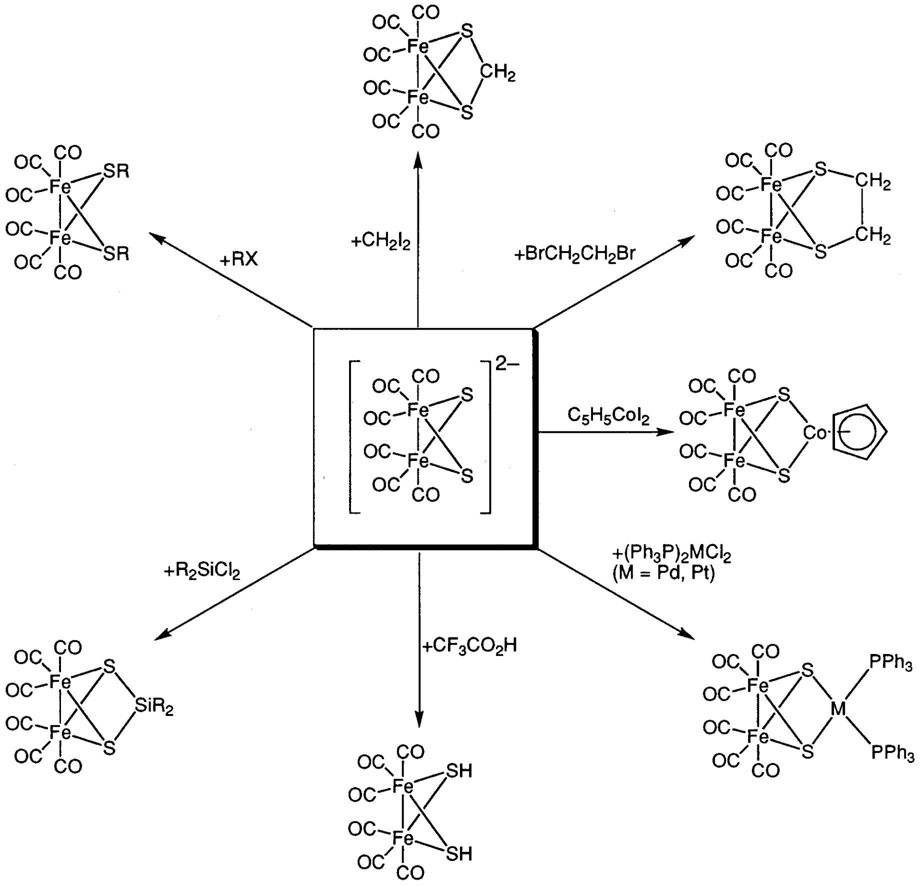

Fig. 5. Some examples of chemical reactions of the dianion $Fe_2(CO)_6S_2^{2-}$.

Fe_2S_2 core is retained. Compounds of the form $Fe_2(CO)_6(\mu\text{-}SR)_2$ exist as either *anti* or *syn* conformers, and these conformers may occasionally be separated using careful chromatographic techniques [40,41]. In the absence of a S–S bond the LUMO for these organosulfide compounds is associated with Fe–Fe antibonding and this shift of the location of nucleophilic attack has significant consequences for the subsequent chemistry.

Substitution of carbonyl ligands by phosphines and phosphites in $Fe_2(CO)_6(\mu\text{-}SR)_2$ and $Fe_2(CO)_6(\mu\text{-}S_2Z)$ derivatives has been established for a wide range of derivatives. In all cases, monosubstitution occurs in the axial position *trans* to the Fe–Fe bond, and disubstitution by monodentate ligands results in predominantly axial/axial substitution [42,43]. In most cases, room temperature or slightly elevated temperatures (60°C) are sufficient to cause ligand exchange, but in the case of larger or less basic ligands photochemical methods may need to be employed.

The kinetics of carbonyl substitution reactions for a large group of $Fe_2(CO)_6(\mu\text{-}SR)_2$ and $Fe_2(CO)_6(\mu\text{-}S_2Z)$ compounds have been examined. In this connection substitution reactions for $Fe_2(CO)_6(\mu\text{-}SR)_2$ derivatives are complicated by *syn–anti* equilibria although it was possible to establish that second-order rate laws hold for these compounds. For compounds of the form $Fe_2(CO)_6(\mu\text{-}S_2Z)$ in which the sulfur atoms are linked by a Z bridge and thus the stereochemistry is fixed, the kinetics yielded clean second-order rate laws. It was found that the rate of carbonyl substitution is a function of ligand size (cone angle) with some very large phosphines such as P(*o*-tolyl)$_3$ and P(cyclohexyl)$_3$ being unreactive under thermal conditions. It was also found that the steric bulk of the organic groups linking the sulfur atoms also effects the rate of reaction with $Fe_2(CO)_6(\mu\text{-}1,2\text{-}S_2C_6H_3\text{-}4\text{-}Me)$ reacting faster than $Fe_2(CO)_6(\mu\text{-}S_2C_2H_4)$.

Substitution of carbonyl groups in $Fe_2(CO)_6(\mu\text{-}SR)_2$ and $Fe_2(CO)_6(\mu\text{-}S_2Z)$ compounds by phosphine ligands increases the electron density of the Fe–Fe bond making it susceptible to attack by electrophiles such as H^+ (see Ref. [44,45]), mercuric salts [46], and SO_2 [47,48]. In all cases the electrophiles are found to bridge the Fe–Fe bond.

Halogenation of $Fe_2(CO)_4L_2(\mu\text{-}SR)_2$ derivatives for a variety of R and L groups results in formation of stable cationic species with a Fe–X–Fe bridge. Similar halogenation reactions of monosubstituted and unsubstituted compounds form short-lived halogen bridged intermediates that react with halide ions to give products of the general formula $Fe_2(CO)_4L_2X_2(\mu\text{-}SR)_2$. The only sulfur linked compound studied, $Fe_2(CO)_6(\mu\text{-}S_2C_2H_4)$, reacts with I_2 to give an isolable species that is formulated as either $[Fe_2(CO)_6(\mu\text{-}I)(\mu\text{-}S_2C_2H_4)](FeI_4)$ or $[Fe_2(CO)_6(\mu\text{-}FeI_4)(\mu\text{-}S_2C_2H_4)]I$. This compound curiously reacts with iodide to reform the neutral compound [49]. Reaction of $Fe_2(CO)_4L_2(\mu\text{-}SPh)_2$ with S_2Ph_2 and $AgPF_6$ yields $[Fe_2(CO)_6(\mu\text{-}SPh)_3]PF_6$ [50,51].

As noted above, photochemical ligand substitution of $Fe_2(CO)_6(\mu\text{-}SR)_2$ and $Fe_2(CO)_6(\mu\text{-}S_2Z)$ is the preferred, and in some cases the only, method for preparing these derivatives for large cone angle phosphines. Photolysis of $Fe_2(CO)_6(\mu\text{-}X)_2$, where X = SMe, SPh, and PMe_2, with activated acetylenes such as $CF_3C{\equiv}CCF_3$ and $MeO_2CC{\equiv}CCO_2Me$ yields products in which the acetylene ligand bridges the two irons in a parallel manner [52]. Similarly, the photochemical reaction of C_2F_4 with $Fe_2(CO)_6(\mu\text{-}SMe)_2$ yields $Fe_2(CO)_6(\mu\text{-}C_2F_4)(\mu\text{-}SMe)_2$ and its thermal rearrangement product, $Fe_2(CO)_6(\mu\text{-}CFCF_3)(\mu\text{-}SMe)_2$ [53]. Photolysis of these iron–sulfur compounds with common organic acetylenes does not yield isolable products [54].

Photochemical studies of $Fe_2(CO)_6(\mu\text{-}SR)_2$ and $Fe_2(CO)_6(\mu\text{-}S_2Z)$ compounds in frozen Nujol at ca. 90 K have established that no detectable photochemistry occurs when the low energy 450 nm absorption bands are activated, but that axial-CO loss occurs upon photolysis into higher energy bands at about 330 nm. These CO-loss photointermediates are certainly the reactive species responsible for ligand substitution and reactions with activated acetylenes.

In the cases of $Fe_2(CO)_6(\mu\text{-}SMe)_2$, $Fe_2(CO)_6(\mu\text{-}S_2CH_2)$, and $Fe_2(CO)_6(\mu\text{-}S_2C_3H_6)$, a second photochemical process is observed at high energy in which the molecule rearranges without CO loss to a structural isomer having bridging or semi-bridging

CO groups. Identical species have been isolated by Alper in which an adamantyl group bridges two sulfur atoms [55]. It is believed that an identical bridging structure is an intermediate in the rapid carbonyl exchange that is observed in the ^{13}C-NMR of these compounds. It is not yet clear what combination of structural factors results in the stabilization of the bridged intermediate since compounds with one and three carbon links between the sulfur atoms yield observable species (at ca. 90 K), yet the two-carbon linked molecule does not.

2.3. Iron carbonyl selenides and tellurides

The corresponding iron carbonyl selenide cluster $Fe_2(CO)_6Se_2$ was originally obtained by reaction of $Fe(CO)_5$ with alkali and polyselenide followed by acidification analogous to the preparation of $Fe_2(CO)_6S_2$ discussed above [16]. A more convenient preparation, which minimizes the generation of large amounts of highly toxic and malodorous H_2Se, uses the reaction between the trinuclear iron cluster $Fe_3(CO)_9Se_2$ and sodium methoxide followed by acidification [56]. Determination of the structure of $Fe_2(CO)_6Se_2$ by X-ray diffraction [57] indicates a structure analogous to that of $Fe_2(CO)_6S_2$ with a Fe–Fe bond length of 2.575(2) Å, an Se–Se bond length of 2.293(2) Å, and an average Fe–Se bond length of 2.364 Å.

The chemistry of the $Fe_2(CO)_6Se_2$ cluster appears to be rather similar to that of the $Fe_2(CO)_6S_2$ cluster discussed above [58,59]. For example, reaction of $Fe_2(CO)_6Se_2$ with two molar equivalents of $LiBEt_3H$ generates the dianion $Fe_2(CO)_6Se_2^{2-}$, which exhibits similar chemical reactivity to its sulfur analogue (Fig. 5) [60].

The orange tellurium analogue $Fe_2(CO)_6Te_2$ is also known but it is considerably less stable than $Fe_2(CO)_6Se_2$ and could not be purely isolated in the solid-state [61]. The instability of $Fe_2(CO)_6Te_2$ appears to be a consequence of the greater lability of the Te–Te bond relative to Se–Se and S–S bonds in corresponding environments. The lability of the Te–Te bond in $Fe_2(CO)_6Te_2$ facilitates opening the Fe_2Te_2 tetrahedron in $Fe_2(CO)_6Te_2$ to the corresponding rhombus, even under ambient conditions, which then leads to immediate dimerization to the corresponding black crystalline nearly insoluble $Fe_4(CO)_{12}Te_4$ cube (Fig. 2, E = Te). The best preparation of $Fe_2(CO)_6Te_2$ uses the reaction of $Fe_3(CO)_9Te_2$ with sodium methoxide in methanol followed by acidification similar to the preparation of $Fe_2(CO)_6Se_2$ discussed above [14]. The required $Fe_3(CO)_9Te_2$ precursor is readily obtained by reactions of basic iron carbonyl solutions with TeO_3^{2-} followed by acidification [16].

3. Chemistry of iron carbonyl phosphinidene clusters: $Fe_2(CO)_6(PR)_2$ and related species

3.1. The t-butyl derivative $Fe_2(CO)_6(P^tBu)_2$

The use of phosphinidene groups RP instead of chalcogen atoms (S, Se, or Te) as the bridges in $Fe_2(CO)_6E_2$ complexes (Fig. 2, E = RP rather than S, Se, or Te) has the potential to modify the chemical reactivity of the Fe_2E_2 unit by varying the steric and electronic properties of the R group. However, in practice, the syntheses of isolable products of the type $Fe_2(CO)_6(PR)_2$ with P–P bonds in the Fe_2P_2 tetrahedron have proven difficult and the only such Fe_2P_2 tetrahedron which has been studied in any detail is the *tert*-butyl derivative $Fe_2(CO)_6(P^tBu)_2$ [62].

The method for the preparation of the red $Fe_2(CO)_6(P^tBu)_2$ tetrahedron is rather complicated (Fig. 6) [62]. First the mononuclear compound $^tBuPH_2Fe(CO)_4$ is prepared by reaction of $^tBuPH_2$ with $Fe_2(CO)_9$ under mild conditions [63]. Pyrolysis of $^tBuPH_2Fe(CO)_4$ in boiling toluene results in dehydrogenation to give a 56% yield of stereoisomers of $Fe_2(CO)_6(PH^tBu)_2$, which can be separated from the $H_2Fe_3(CO)_9P^tBu$ byproduct (19% yield) by chromatography. Deprotonation of $Fe_2(CO)_6(PH^tBu)_2$ with methyllithium in diethyl ether followed by addition of 1,2-dibromoethane was found to give a 55% yield of $Fe_2(CO)_6(P^tBu)_2$ (Fig. 6).

The P–P bond in $Fe_2(CO)_6(P^tBu)_2$ is reactive towards insertion reactions in thermal reactions at 80°C, particularly under pressure, without the need for photolysis (Fig. 6) [62]. Insertions of ethylene and CO similar to those observed for $Fe_2(CO)_6S_2$ (Fig. 3) can be effected under such conditions [62]. Reaction of $Fe_2(CO)_6(P^tBu)_2$ with H_2 at 80°C/50 atmospheres regenerates the $Fe_2(CO)_6(PH^tBu)_2$

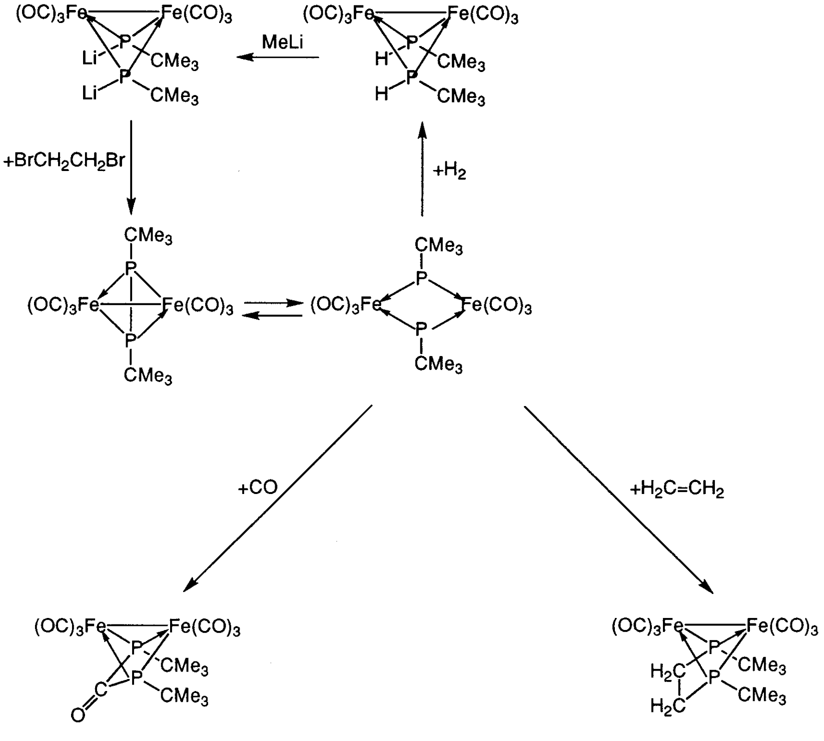

Fig. 6. Synthesis and chemical reactivity of the Fe_2P_2 tetrahedron $Fe_2(CO)_6(P^tBu)_2$.

stereoisomeric mixture, which was an intermediate in the original preparation of $Fe_2(CO)_6(P^tBu)_2$ (Fig. 6).

3.2. Dialkylaminophosphorus iron carbonyl derivatives

Reactions of bulky R_2NPCl_2 derivatives with $Na_2Fe(CO)_4$ in ethereal solvents have not yet been found to provide any isolable $Fe_2(CO)_6(PNR_2)_2$ tetrahedranes but instead provide other entries into the same types of products obtained from reactions of $Fe_2(CO)_6E_2$ tetrahedra. Of particular interest is the orange air-stable phosphorus-bridging carbonyl derivative $(^iPr_2NP)_2COFe_2(CO)_6$ (Fig. 7(a)), which can be obtained in yields up to 40% by the reaction of $^iPr_2NPCl_2$ with $Na_2Fe(CO)_4$ in diethyl ether [64,65]. This synthesis can be run on a relatively large scale using inexpensive raw materials ($^iPr_2NH$, PCl_3, $Fe(CO)_5$ and sodium) so that $(^iPr_2NP)_2COFe_2(CO)_6$ is a readily available iron carbonyl derivative, whose chemistry has been studied in some detail [66–69].

The aspect of the chemistry of $(^iPr_2NP)_2COFe_2(CO)_6$ of interest in the context of this paper is its thermal reactivity with unsaturated organic molecules (Fig. 7(a)) [70]. Thus heating $(^iPr_2NP)_2COFe_2(CO)_6$ with a variety of unsaturated organic compounds at 80–100°C leads to extrusion of the phosphorus-bridging carbonyl group followed by apparent addition of the resulting $Fe_2(CO)_6(PN^iPr_2)_2$ unit across a multiple bond of the unsaturated organic compound. In this way addition reactions of the $Fe_2(CO)_6(PN^iPr_2)_2$ unit to the C=O bonds of aldehydes and ketones [71] and the C≡N bonds of nitriles [70] to give air-stable organometallic products have been achieved (Fig. 7a). A similar thermal reaction of acrylonitrile with $(^iPr_2NP)_2COFe_2(CO)_6$ leads to addition of the C=C rather than the C≡N bond to the resulting $Fe_2(CO)_6(PN^iPr_2)_2$ unit. More surprisingly, the thermal reaction of maleic anhydride with $(^iPr_2NP)_2COFe_2(CO)_6$ leads to addition of a C=O bond rather than the C=C bond to the $Fe_2(CO)_6(PN^iPr_2)_2$ unit even though maleic anhydride is a good dienophile for the Diels–Alder reaction through its C=C bond. The thermal reaction of $(^iPr_2NP)_2COFe_2(CO)_6$ with ethyl cyanoacetate results in addition of its ketenimine tautomer $HN{=}C{=}CHCO_2Et$ to the $Fe_2(CO)_6(PN^iPr_2)_2$ unit (Fig. 7(a)). Norbornadiene forms a nortricyclene derivative with $Fe_2(CO)_6(PN^iPr_2)_2$ but this reaction is more complicated than the other reactions in Fig. 7(a) since one of the $^iPr_2N$ groups is lost in the norbornadiene/$Fe_2(CO)_6(PN^iPr_2)_2$ reaction.

The nature of the products in all of these thermal reactions of $(^iPr_2NP)_2COFe_2(CO)_6$ suggested the intermediacy of a tetrahedrane $Fe_2(CO)_6(PN^iPr_2)_2$ analogous to the $Fe_2(CO)_6(P^tBu)_2$ discussed above. In an attempt to isolate such a tetrahedrane, solutions of $(^iPr_2NP)_2COFe_2(CO)_6$ in inert organic solvents (e.g. toluene) were heated to the reaction temperature (e.g. 80–100°C) in the absence of a substrate. However, no evidence was obtained for formation of an isolable $Fe_2(CO)_6(PN^iPr_2)_2$ under such conditions. No tractable intermediates could be isolated at temperatures and reaction times where decomposition of $(^iPr_2NP)_2COFe_2(CO)_6$ was first observed. Furthermore, photolysis of $(^iPr_2NP)_2COFe_2(CO)_6$ at ambient conditions in an inert solvent failed to give any evidence of an isolable tetrahedrane $Fe_2(CO)_6(PN^iPr_2)_2$.

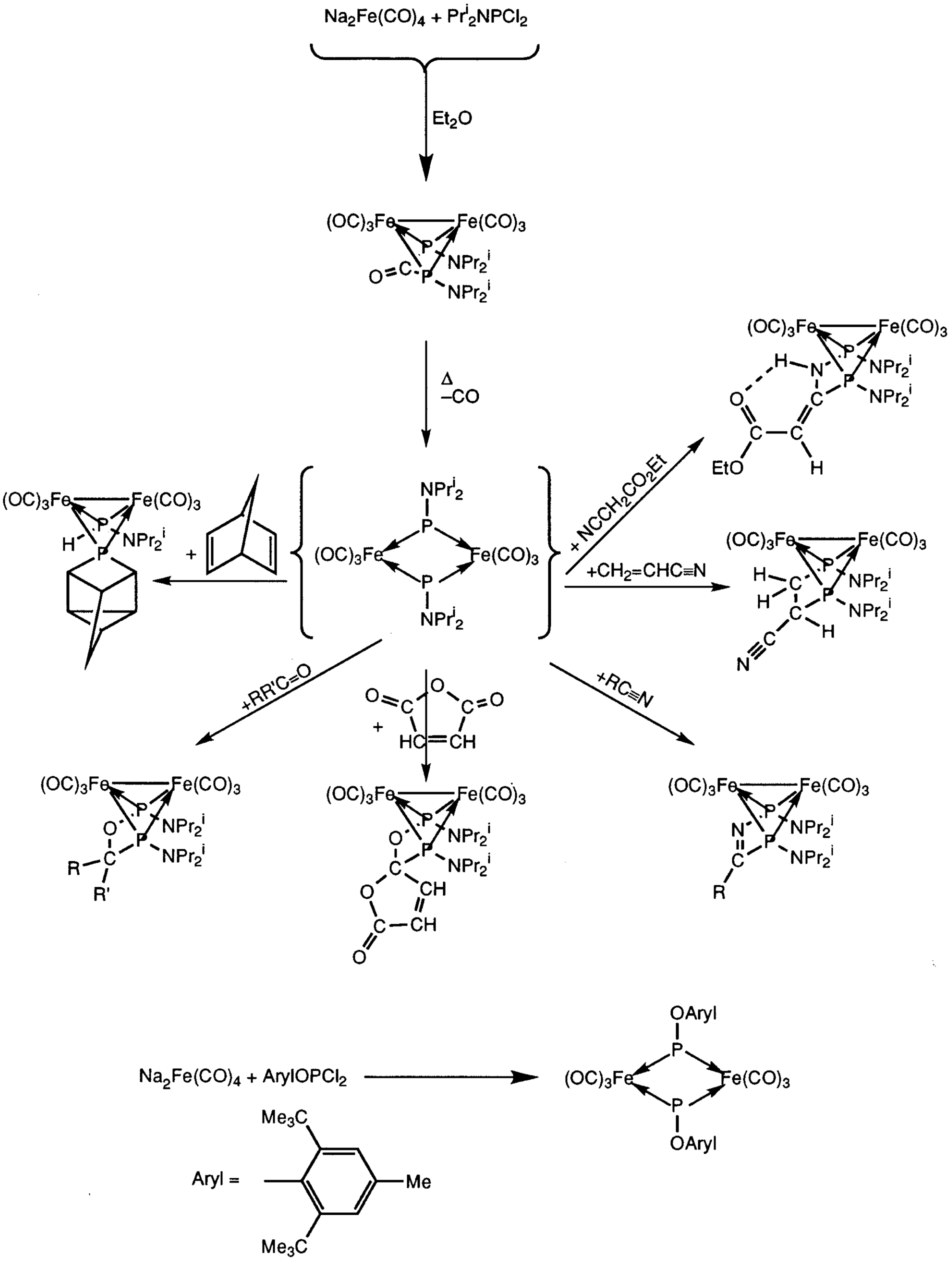

Fig. 7. (a) Synthesis and chemical reactivity of the phosphorus-bridging carbonyl $(^{i}Pr_2NP)_2COFe_2(CO)_6$ towards some unsaturated organic molecules. (b) Synthesis of a stable $Fe_2(CO)_6(POR)_2$ rhombus.

The nature of this specific system was recently clarified by a matrix isolation study involving low-temperature photolysis of $(^i\mathrm{Pr_2NP})_2\mathrm{COFe_2(CO)_6}$ in a Nujol medium using well-established experimental techniques [72]. During the course of such a low-temperature photolysis the original ν(CO) bands of the $\mathrm{Fe_2(CO)_6}$ unit in $(^i\mathrm{Pr_2NP})_2\mathrm{COFe_2(CO)_6}$ were replaced by a new set of ν(CO) bands, which could be interpreted as two $\mathrm{Fe(CO)_3}$ groups in an environment of significantly higher symmetry (e.g. D_{4h}) than in the $(^i\mathrm{Pr_2NP})_2\mathrm{COFe_2(CO)_6}$ starting material [73]. This provides important spectroscopic evidence for a nearly square $\mathrm{Fe_2P_2}$ rhombus [8] having neither Fe–Fe nor P–P bonds in the $\mathrm{Fe_2(CO)_6(PN^iPr_2)_2}$ intermediate generated by photolysis of $(^i\mathrm{Pr_2NP})_2\mathrm{COFe_2(CO)_6}$. The same $\mathrm{Fe_2(CO)_6(PN^iPr_2)_2}$ rhombus is presumably involved in the thermal reactions of $(^i\mathrm{Pr_2NP})_2\mathrm{COFe_2(CO)_6}$ with the unsaturated organic compounds in Fig. 7(a) rather than the butterfly-shaped intermediate retaining the Fe–Fe bond proposed in previous reports of these reactions [67–70]. Thus photochemical and probably thermal extrusion of the phosphorus-bridging CO group in $(^i\mathrm{Pr_2NP})_2\mathrm{COFe_2(CO)_6}$ appears to involve concurrent rupture of its Fe–Fe bond. The resulting $\mathrm{Fe_2(CO)_6(PN^iPr_2)_2}$ rhombus does not appear to close to a stable $\mathrm{Fe_2(CO)_6(PN^iPr_2)_2}$ tetrahedron analogous to $\mathrm{Fe_2(CO)_6(P^tBu)_2}$ (Fig. 6).

3.3. A stable $\mathrm{Fe_2(CO)_6(POR')_2}$ rhombus

The postulation of coordinatively unsaturated rhombus photointermediates $\mathrm{Fe_2(CO)_6E_2}$ (E = S, Se, Te) to account for much of their chemical reactivity (Fig. 2) makes of particular significance the isolation and characterization of a stable compound with a related $\mathrm{Fe_2E_2}$ rhombus structure. Such an $\mathrm{Fe_2(CO)_6(PR)_2}$ rhombus in which the R group is a very bulky aryloxy group, namely 2,6-di-*tert*-butyl-4-methylphenoxy, was discovered, apparently serendipitously, by Power and co-workers [15] as an unexpected product during their studies of reactions of various $\mathrm{RPCl_2}$ derivatives with $\mathrm{Na_2Fe(CO)_4}$. Thus reaction of 2,6-$^t\mathrm{Bu_2}$-4-Me-$\mathrm{C_6H_2OPCl_2}$ with $\mathrm{Na_2Fe(CO)_4}$ in diethyl ether under conditions similar to those used for the preparation of $(^i\mathrm{Pr_2NP})_2\mathrm{COFe_2(CO)_6}$ from $\mathrm{Na_2Fe(CO)_4}$ and $^i\mathrm{Pr_2NPCl_2}$ was found to give a 9% yield of red–brown air-stable $\mathrm{Fe_2(CO)_6(POC_6H_2\text{-}4\text{-}Me\text{-}2,6\text{-}{}^tBu_2)_2}$ (Fig. 7(b)). Determination of the structure of this complex by X-ray diffraction indicates the presence of a planar $\mathrm{Fe_2P_2}$ rhombus with P–Fe–P angles of 66.5(1)° and Fe–P–Fe angles of 113.5(1)°. Presumably the large steric bulk of the 2,6-di-*tert*-butyl-4-methylphenoxy substituents on the phosphorus atoms inhibits the dimerization of this $\mathrm{Fe_2P_2}$ rhombus to the corresponding $\mathrm{Fe_4P_4}$ cube (Fig. 2).

4. Summary

Many iron–sulfur metalloenzymes are based on $\mathrm{Fe_4S_4}$ cubes in which the iron sites have high-spin tetrahedral coordination. Such $\mathrm{Fe_4S_4}$ cubes can be obtained by dimerization of $\mathrm{Fe_2S_2}$ rhombuses. Similar cluster aggregation processes can be observed for model Fe–S systems in which the high-spin tetrahedral iron sites are replaced by low-spin octahedral $Fe(CO)_3S_3$ sites. The Fe_2S_2 analogue for the metal carbonyl system is $Fe_2(CO)_6S_2$, whose ground-state structure contains a Fe_2S_2 tetrahedron with Fe–Fe and S–S bonds as well as four Fe–S bonds. However, much of the observed photochemistry of $Fe_2(CO)_6S_2$ can be rationalized by a coordinatively unsaturated rhombus photointermediate in which the Fe–Fe and S–S bonds of the ground state have broken in a concerted process in accord with molecular orbital calculations.

Additional insight into the chemistry of these iron carbonyl sulfides is obtained by replacement of the sulfur atoms by isoelectronic RP groups. Thus the stable $Fe_2(CO)_6(P^tBu)_2$ tetrahedron can be isolated and characterized; it exhibits similar chemical reactivity to $Fe_2(CO)_6S_2$ towards substrates such as CO and olefins, albeit under thermal rather than photochemical conditions. Other stable $Fe_2(CO)_6(PR)_2$ tetrahedra do not appear to be known but there are other ways into related $Fe_2(PR)_2$ chemistry. For example, the reaction of $Na_2Fe(CO)_4$ with $^iPr_2NPCl_2$ gives the phosphorus-bridging carbonyl derivative $(^iPr_2NP)_2COFe_2(CO)_6$, which undergoes thermal reactions with unsaturated organic molecules to give adducts of their C=C, C=O, or C≡N bonds to the phosphorus atoms of a $Fe_2(CO)_6(PN^iPr_2)_2$ unit generated by extrusion of the phosphorus-bridging carbonyl group. Attempts to isolate the tetrahedrane $Fe_2(CO)_6(PN^iPr_2)_2$ by thermolysis or photolysis of $(^iPr_2NP)_2COFe_2(CO)_6$ in an inert organic solvent in the absence of a substrate have so far been unsuccessful. However, a low-temperature infrared spectroscopic study of $(^iPr_2NP)_2COFe_2(CO)_6$ photolyzed in a Nujol matrix provides evidence for an unstable $Fe_2(CO)_6(PN^iPr_2)_2$ rhombus of high symmetry. In addition, reaction of $Na_2Fe(CO)_4$ with 2,6-$^tBu_2$-4-Me-$C_6H_2OPCl_2$ has been found to give the stable Fe_2P_2 rhombus $Fe_2(CO)_6(POC_6H_2\text{-4-Me-2,6-}^tBu_2)_2$, whose structure has been confirmed by X-ray diffraction.

References

[1] W. Lovenberg (Ed.), Iron–Sulfur Proteins, vols. I and II, Academic Press, New York, 1973.

[2] T.G. Spiro (Ed.), Iron–Sulfur Proteins, Wiley, New York, 1982.

[3] H. Beinert, FASEB J. 4 (1990) 2483.

[4] R. Cammack, A.G. Sykes (Eds.), Iron–Sulfur Proteins, Academic Press, San Diego, CA, 1992.

[5] H. Beinert, R.H. Holm, E. Munck, Science 277 (1997) 653.

[6] J.S. Kim, D.C. Rees, Science 257 (1992) 1677.

[7] J.W. Peters, W.N. Lanzilotta, B.J. Lemon, L.C. Seefeldt, Science 282 (1998) 1853.

[8] Recall that a rhombus is a quadrilateral with all four sides equal but with the four angles not necessarily 90° in contrast to a square where all four angles must be 90° in addition to all sides being equal. The coordination geometries of the iron and sulfur atoms in the proposed $Fe_2(CO)_6S_2$ photointermediate without Fe–Fe and S–S bonds do not require that the S–Fe–S and Fe–S–Fe bond angles be 90° so that the structure of this proposed intermediate is best described as a rhombus rather than a square.

[9] R.H. Holm, Chem. Soc. Rev. 10 (1981) 455.

[10] R.H. Holm, Acc. Chem. Res. 10 (1977) 427.

[11] R.W. Lane, J.A. Ibers, R.B. Frankel, G.C. Papaefthymiou, R.H. Holm, J. Am. Chem. Soc. 99 (1977) 84.

[12] L. Noodleman, C.Y. Peng, D.A. Case, J.-M. Mouesca, Coord. Chem. Rev. 144 (1995) 199.
[13] C.V. Popescu, E. Münck, J. Am. Chem. Soc. 121 (1999) 7877.
[14] L.E. Bogan Jr., D.A. Lesch, T.B. Rauchfuss, J. Organomet. Chem. 250 (1983) 429.
[15] K.M. Flynn, R.A. Bartlett, M.M. Olmstead, P.P. Power, Organometallics 5 (1986) 813.
[16] W. Hieber, J. Gruber, Z. Anorg. Allgem. Chem. 296 (1958) 91.
[17] D. Seyferth, R.S. Henderson, L.-C. Song, Organometallics 1 (1982) 125.
[18] C.H. Wei, L.F. Dahl, Inorg. Chem. 4 (1965) 1.
[19] I.L. Eremenko, H. Berke, A.A.H. van der Zeijden, B.I. Kolobkov, V.M. Novotorstev, J. Organomet. Chem. 471 (1994) 123.
[20] R.L. De Kock, E.J. Baerends, A. Oskam, Inorg. Chem. 22 (1983) 4158.
[21] H. Kunkely, A. Vogler, J. Organomet. Chem. 568 (1998) 291.
[22] J. Messelhäuser, I.-P. Lorenz, K. Haug, W. Hiller, Z. Naturforsch. Teil B 40 (1985) 1064.
[23] J. Messelhäuser, K.U. Gutensohn, I.-P. Lorenz, W. Hiller, J. Organomet. Chem. 321 (1987) 377.
[24] A. Kramer, I.-P. Lorenz, J. Organomet. Chem. 388 (1990) 187.
[25] A. Kramer, R. Lingnau, I.-P. Lorenz, H.A. Mayer, Chem. Ber. 123 (1990) 1821.
[26] R.B. King, M.B. Bisnette, Inorg. Chem. 4 (1965) 1663.
[27] L.L. Nelson, F.Y.-K. Lo, A.D. Rae, L.F. Dahl, J. Organomet. Chem. 225 (1982) 309.
[28] T.E. Bitterwolf, J.T. Bays, C.A. Weiss, W.B. Scallorn, J.L. Johnson, submitted for publication.
[29] N.S. Nametkin, B.I. Kolobkhov, V.D. Tyurin, A.N. Muratov, A.I. Nekhaev, M.Yu. Mavlonov, A. Sideridu, G.G. Aleksandrov, A.V. Lebedev, M.T. Tashev, H.B. Dustov, J. Organomet. Chem. 276 (1984) 393.
[30] R. Rossetti, G. Gervasio, P.L. Stanghellini, Inorg. Chem. Acta 35 (1979) 73.
[31] S. Aime, G. Gervasio, R. Rossetti, P.L. Stanghellini, Inorg. Chem. Acta. 40 (1980) 131.
[32] G. Cetini, P.L. Stanghellini, R. Rossetti, O. Gambino, Inorg. Chem. Acta 2 (1968) 433.
[33] W. Hieber, K. Kaiser, Chem. Ber. 102 (1969) 4043.
[34] K.S. Bose, E. Sinn, B.A. Averill, Organometallics 3 (1984) 1126.
[35] D. Seyferth, R.S. Henderson, J. Organomet. Chem. 218 (1981) C34.
[36] D. Seyferth, R.S. Henderson, M.K. Gallagher, J. Organomet. Chem. 193 (1980) C75.
[37] P.A. Eldredge, B.A. Averill, J. Cluster Sci. 1 (1990) 269.
[38] P.A. Eldredge, K.S. Bose, D.E. Barber, R.F. Bryan, E. Sinn, A. Rheingold, Inorg. Chem. 30 (1991) 2365.
[39] R.B. King, J. Am. Chem. Soc. 84 (1962) 2460.
[40] G. Bor, J. Organomet. Chem. 11 (1968) 195.
[41] J.A. de Beer, R.J. Haines, R. Greatrex, N.N. Greenwood, J. Chem. Soc. A (1971) 3271.
[42] J.A. de Beer, R.J. Haines, J. Organomet. Chem. 36 (1972) 297.
[43] K. Fauvel, R. Mathieu, R. Poilblanc, Inorg. Chem. 15 (1976) 976.
[44] M.S. Arabi, R. Mathieu, R. Poilblanc, J. Organomet. Chem. 177 (1979) 199.
[45] M.S. Arabi, R. Mathieu, R. Poilblanc, Inorg. Chem. Acta 23 (1977) L17.
[46] M.S. Arabi, R. Mathieu, R. Poilblanc, Inorg. Chem. Acta. 34 (1979) L207.
[47] N.J. Taylor, M.S. Arabi, R. Mathieu, Inorg. Chem. 19 (1980) 1740.
[48] R.J. Haines, J.A. de Beer, R. Greatrex, J. Chem. Soc. Dalton Trans. (1976) 1749.
[49] A.J. Schultz, R. Eisenberg, Inorg. Chem. 12 (1973) 518.
[50] C.J. Jones, J.A. McCleverty, J. Chem. Soc. Dalton Trans. (1975) 701.
[51] R. Mathieu, R. Poilblanc, J. Organomet. Chem. 142 (1977) 351.
[52] J.J. Bonnet, R. Mathieu, R. Poilblanc, J.A. Ibers, J. Am. Chem. Soc. 101 (1979) 7487.
[53] T.E. Bitterwolf, unpublished results.
[54] H. Alper, A.S.K. Chan, Inorg. Chem. 13 (1974) 232.
[55] P. Mathur, D. Chakrabarty, M.M. Hossain, R.S. Rashid, V. Rugmini, A.L. Rheingold, Inorg. Chem. 31 (1992) 1106.
[56] C.F. Campana, F.Y.-K. Lo, L.F. Dahl, Inorg. Chem. 18 (1979) 3060.
[57] L.C. Roof, J.W. Kolis, Chem. Rev. 93 (1993) 1037.
[58] P. Mathur, Adv. Organomet. Chem. 41 (1997) 243.
[59] D. Seyferth, R.S. Henderson, J. Organomet. Chem. 204 (1981) 333.
[60] D.A. Lesch, T.B. Rauchfuss, Inorg. Chem. 20 (1981) 3583.

[61] R.L. De, D. Wolters, H. Vahrenkamp, Z. Naturforsch. Teil B 41 (1986) 283.
[62] H. Vahrenkamp, E.J. Wucherer, D. Wolters, Chem. Ber. 116 (1983) 1219.
[63] R.B. King, F.-J. Wu, N.D. Sadanani, E.M. Holt, Inorg. Chem. 24 (1985) 4449.
[64] R.B. King, F.J. Wu, E.M. Holt, J. Am. Chem. Soc. 109 (1987) 7764.
[65] R.B. King, F.-J. Wu, E.M. Holt, J. Organomet. Chem. 383 (1990) 295.
[66] R.B. King, Synlett (1991) 671.
[67] R.B. King, Russ. Chem. Bull. 42 (1993) 1858.
[68] R.B. King, J. Organomet. Chem. 557 (1998) 29.
[69] Y.W. Li, M.G. Newton, R.B. King, Inorg. Chem. 32 (1993) 5720.
[70] R.B. King, N.K. Bhattacharyya, E.M. Holt, J. Organomet. Chem. 421 (1991) 247.
[71] A.J. Rest, J. Mol. Struct. 222 (1990) 87.
[72] T.E. Bitterwolf, unpublished results.