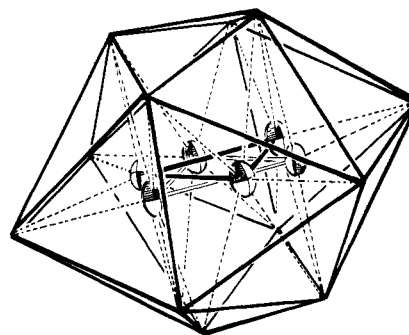Figure 2. The polyhedron defined by the peripheral oxygen atoms of the $Os_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}CH_2)$ structure. Note that any one molecule can only be associated with 11 carbonyl groups and therefore contains only 11 oxygen atoms.

Figure 1. (A) Complete disordered structure. (B) Labeling of atoms in the composite image of two mirror-related $Os_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}CH_2)$ molecules showing disorder of the bridging carbonyl and methylene groups. The philosophy behind the labeling is as follows: (a) one Os_3 triangle is chosen; (b) the six unique oxygen atoms are labeled with the first digit identical with the nonprimed osmium atom to which they are joined; (c) the two $^1/_2$-carbon atoms associated with a given oxygen atom are labeled a and b; (d) all atoms related to the basic set by inversion about (0, 0, 0) are labeled with a prime. Note that C(11') and C(12') are the composite of disordered methylene and carbonyl carbon atoms (see text).

= 2.677 (2) and 2.683 (1) Å.

(2) The overall molecular skeleton is very similar to that found in a variety of $Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}L)$ complexes.[15]

(3) The outer oxygen atoms define a geometric figure that is a distorted icosahedron (Figure 2). A similar figure is defined by the oxygen atoms of $Fe_3(CO)_{12}$, whereas the oxygen atoms of both $Os_3(CO)_{12}$[14] and $Ru_3(CO)_{12}$[16] define an alternative symmetrical geometric figure—the anticuboctahedron, which does not possess an inversion center.

(4) The osmium–(bridging ligand) distances range from 2.311 (23) to 2.434 (34) Å; one suspects that the esd's associated with the distances are far too small. Atoms C(11), C(12), C(11'), C(12') are, in any case, the composites of disordered bridging ligands across Os(2)–Os(3) and Os-(2')–Os(3') and terminal carbonyl carbon atoms on Os(1) and Os(1'). In known ordered structures, the Os–C (carbene) distances in $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}CHCH_2PMe_2Ph)$ are 2.148 (9) and 2.173 (8) Å,[17] while those in $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}$

$CHCH=NEt_2)$ are 2.15 (3) and 2.16 (3) Å.[18] One would expect Os–$(\mu\text{-}CO)$ distances of ~2.1 Å.[19,20]

Registry No. $Os_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}CH_2)$, 77208-32-3.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes (7 pages). Ordering information is given on any current masthead page.

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(19) The crystal structure of the related ordered species $Os_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}CHSiMe_3)$ has now been completed (see ref 20). All aspects of this structure are in keeping with our proposals for $Os_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}CH_2)$.
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Contribution from the School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801

Roussin's Red Salt Revisited: Reactivity of $Fe_2(\mu\text{-}E)_2(NO)_4^{2-}$ (E = S, Se, Te) and Related Compounds

Thomas B. Rauchfuss* and Timothy D. Weatherill

Salts of $Fe_2(\mu\text{-}S)_2(NO)_4^{2-}$ were first synthesized in 1858 by Roussin in an attempt to prepare analogues of the nitroprusside ion.[1] It was not until much later[2] that the structure of "Roussin's red salt" was deduced by analogy to its esters, $Fe_2(\mu\text{-}SR)_2(NO)_4$,[3] and the thiosulfate $Fe_2(\mu\text{-}S_2O_3)_2(NO)_4^{2-}$.[4] In 1958, the X-ray structures of both the ethyl ester[5] and the "black salt" $Cs[Fe_4(\mu_3\text{-}S)_3(NO)_7]H_2O$[6] were published. Since that time these compounds have elicited little interest from the inorganic community despite intense activity in the areas

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Table I. Analytical Data^a

compd	% C	% H	% N
Fe$_2$(μ-SCH$_2$Ph)$_2$(NO)$_4$	35.32 (35.17)	2.95 (2.95)	11.81 (11.72)
Fe$_2$(μ-SCH$_2$CH$_2$CH$_2$Br)$_2$(NO)$_4$	13.74 (13.35)	2.31 (2.24)	13.33 (10.38)
Fe$_2$(μ-SPh)$_2$(NO)$_4$	32.20 (32.82)	2.13 (2.24)	12.66 (12.45)
Fe$_2$(μ-SePh)$_2$(NO)$_4$	26.56 (26.50)	2.05 (1.85)	10.83 (10.30)
Fe$_2$(μ-SeCH$_2$Ph)$_2$(NO)$_4$	29.10 (29.40)	2.48 (2.47)	9.14 (9.80)
Fe$_2$(μ-TePh)$_2$(NO)$_4$	22.98 (22.48)	1.51 (1.57)	8.11 (8.74)
Fe$_2$(μ-TeCH$_2$Ph)$_2$(NO)$_4$	24.15 (25.13)	2.28 (2.11)	8.09 (8.37)
(NO)$_4$Fe$_2$(μ_3-S)$_2$Ni(dppe)	41.89 (41.47)	3.70 (3.21)	7.22 (7.44)

^{a} Calculated values are in parentheses.

of metal nitrosyls and iron–sulfur clusters. Of relevance to Roussin's red salt, Seyferth and co-workers prepared Fe$_2$(μ-S)$_2$(CO)$_6^{2-}$ by reduction of the neutral disulfido compound Fe$_2$(μ-S$_2$)(CO)$_6$.[7] This reaction is proposed to proceed via S–S bond cleavage comparable to the 2e reduction of an organic disulfide. Alkylation and metalation studies suggest that the negative charge is localized on the sulfur atoms (eq 1).[8]

$$\text{(1)}$$
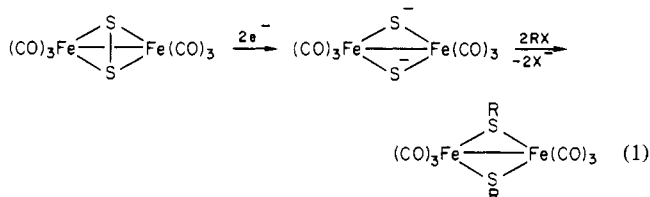
This process is of considerable interest since it indicates that, contrary to theoretical predictions,[9] the LUMO of Fe$_2$(μ-S$_2$)(CO)$_6$ is of S–S σ^* character and *not* metal localized. Such a result holds important ramifications for the understanding of the reactivity of metal chalcogenide cluster compounds, many of which are of interest in catalysis,[10] enzymology,[11,12] and solid-state physics.[13] In contrast to the highly reactive and air-sensitive nature of the anionic *carbonyl* sulfide Fe$_2$-(μ-S)$_2$(CO)$_6^{2-}$, Roussin's *nitrosyl* sulfide is prepared aerobically in boiling 10% potassium hydroxide.[14] This note describes some of our efforts to further delineate the chemistry of this nitrosyl dianion and its analogues.

Experimental Section

^{1}H NMR spectra were obtained on a Varian EM-390 spectrophotometer with Me$_4$Si as an internal reference. IR spectra were obtained on a Perkin-Elmer 599B spectrophotometer on CH$_2$Cl$_2$ solutions. Mass spectra were run on a Varian CH-5 spectrometer, and microanalyses were performed by the School of Chemical Sciences analytical laboratory.

Reactions were performed under nitrogen in reagent grade solvents except for THF, which was freshly distilled from sodium ketyl. Roussin's red salt was prepared from the black salt according to Brauer;[14] Fe$_2$(μ-I)$_2$(NO)$_4$ was prepared according to the literature method.[15]

Alkylation of Roussin's Red Salt: Preparation of Fe$_2$(μ-SCH$_2$Ph)$_2$(NO)$_4$. To 200 mg of K$_2$[Fe$_2$S$_2$(NO)$_4$]·8H$_2$O (0.386 mmol) in 10 mL of CH$_3$CN was added 0.044 mL (48 mg, 0.772 mmol) of

benzyl chloride (Mallinckrodt). Immediately after the addition of the benzyl chloride, thin-layer chromatography on silica gel using CH$_2$Cl$_2$ as elutant showed a single, fast-moving brown spot. After it was stirred for 30 min, the reaction mixture was evaporated, extracted with CH$_2$Cl$_2$, and filtered through a bed of silica gel. The filtrate was reduced in volume, and CH$_3$OH was added to precipitate 168 mg (92% yield) of dark brown microcrystals.

Polymer-Bound Fe$_2$S$_2$(NO)$_4$. Chloromethylated polystyrene (156 mg, 2% cross-linked, 20% Cl) was swelled for 1 h in 5 mL of PhCH$_2$CN. The sodium salt of Roussin's red salt (100 mg) was dissolved in 5 mL of CH$_3$CN and added to the swelled polymer. After it was stirred for 24 h, the mixture was filtered and washed with CH$_3$CN until the filtrate was clear. The tan solid (170 mg) was dried in vacuo at 40 °C. Anal. Found: Fe, 2.05; S, 0.98.

Fe$_2$(μ-EPh)$_2$(NO)$_4$ from Fe$_2$(μ-I)$_2$(NO)$_4$. To a THF solution of 344 mg of Ph$_2$Se$_2$ (1.1 mmol, Aldrich) was added 2.2 mL of a 1 M solution of LiBEt$_3$H (Aldrich).[16] After 15 min the clear solution was cooled to −78 °C and 536 mg of Fe$_2$(μ-I)$_2$(NO)$_4$ (1.1 mmol) was added in one portion. The dark brown solution was allowed to warm to room temperature and stirred overnight. After removal of the THF in vacuo, the residue was extracted with CH$_2$Cl$_2$ and filtered through a bed of silica gel. The filtrate was diluted with CH$_3$OH and concentrated to give 410 mg (75% yield) of brown crystals, which were dried in vacuo at 40 °C. Fe$_2$(μ-TePh)$_2$(NO)$_4$ was prepared similarly from Ph$_2$Te$_2$ while Fe$_2$(μ-SPh)$_2$(NO)$_4$ was prepared from PhSH, Fe$_2$(μ-I)$_2$(NO)$_4$, and Et$_3$N.

Fe$_2$(μ-ECH$_2$Ph)$_2$(NO)$_4$ (E = Se, Te). To 228 mg of Se powder (Aldrich, 2.88 mmol) in 20 mL of THF was added 5.78 mL (5.78 mmol) of a 1 M solution of LiBEt$_3$H. The milky solution was cooled to −78 °C and 700 mg (1.44 mmol) of Fe$_2$(μ-I)$_2$(NO)$_4$ added in one portion. After the solution was warmed at room temperature for 15 min, 0.4 mL (3.4 mmol) of benzyl chloride was added and the mixture was stirred at room temperature for 2 h. The solution was evaporated and the residue extracted with CH$_2$Cl$_2$ and filtered through silica gel. Addition of CH$_3$OH to the filtrate gave 410 mg (50% yield) of brown microcrystals. Fe$_2$(μ-TeCH$_2$Ph)$_2$(NO)$_4$ was prepared similarly from Te powder and isolated as a red-brown powder.

Fe$_2$(μ-PPh$_2$)$_2$(NO)$_4$. To a THF solution of 2.88 mmol of Ph$_2$PLi generated from 0.5 mL of Ph$_2$PH (Strem) and an equimolar amount of n-butyllithium was added 700 mg of Fe$_2$(μ-I)$_2$(NO)$_4$ at −78 °C. The resulting dark red solution was allowed to warm to room temperature and stirred for 2 h. The evaporated reaction mixture was extracted with CH$_2$Cl$_2$ and passed through a bed of silica gel. CH$_3$OH was added to the filtrate, which was concentrated to give 600 mg (70% yield) of red-brown crystals.

Fe$_2$(μ-SCH$_2$Ph)(μ-SePh)(NO)$_4$. To a Schlenk flask charged with 343 mg (1.1 mmol) of Ph$_2$Se$_2$ and 40 mL of THF was added 2.2 mL of 1 M LiBEt$_3$H. After the clear solution was cooled to −78 °C, 1.0 g (2.0 mmol) of Fe$_2$(μ-I)$_2$(NO)$_4$ was added in one portion. The dark brown solution was warmed to ambient temperature and cooled to −78 °C, and a THF solution of 248 mg of PhCH$_2$SH (2.0 mmol) and 300 mg of Et$_3$N was added. After the mixture was warmed to room temperature, the solution was evaporated. The CH$_2$Cl$_2$ extract of the residue was filtered through silica gel, diluted with MeOH, and concentrated to give 700 mg (71% yield) of brown crystals. Anal. Calcd for C$_{13}$H$_{12}$Fe$_2$N$_4$O$_4$SSe: C, 30.56; H, 2.37; N, 10.97. Found: C, 30.85; H, 2.24; N, 10.43. A sample of the crude product was chromatographed on Florisil (100–200 mesh) by eluting with pentane. The second and major band was collected, evaporated, and shown by TLC and ^{1}H NMR to be pure Fe$_2$(μ-SCH$_2$Ph)(μ-SePh)(NO)$_4$.

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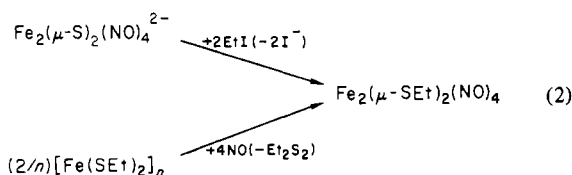
Table II. Spectroscopic Data

compd	IR (ν_{NO}), cm^{-1} ^{a}	^{1}H NMR, δ ^{b}	EI MS (% base)^c
Fe$_2$(μ-SCH$_2$Ph)$_2$(NO)$_4$	1779, 1750	7.30 (s, 5 H), 4.11 (s, 1 H), 4.09 (s, 1 H)	478 (M$^+$, 24.9)
Fe$_2$(μ-SP)$_2$(NO)$_4$^{d}	1772, 1745		
Fe$_2$(μ-SCH$_2$CH$_2$CH$_2$Br)$_2$(NO)$_4$	1775, 1750	3.40 (m, 2 H), 2.90 (m, 2 H), 2.20 (m, 2 H)	510 (M$^+$ − NO, 0.68)
Fe$_2$(μ-SPh)$_2$(NO)$_4$	1780, 1750	7.21 (s), 7.09 (s)	450 (M$^+$, 1.88)
Fe$_2$(μ-SeCH$_2$Ph)$_2$(NO)$_4$	1775, 1750	7.22 (s, 5 H), 4.25 (s, 2 H)	574 (M$^+$, 4.66)
Fe$_2$(μ-SePh)$_2$(NO)$_4$	1775, 1750	7.20 (s), 7.05 (s)	546 (M$^+$, 4.75)
Fe$_2$(μ-TeCH$_2$Ph)$_2$(NO)$_4$	1765, 1745	7.22 (s), 4.60 (s)	674 (M$^+$, 4.59)
Fe$_2$(μ-TePh)$_2$(NO)$_4$	1770, 1750	7.2 (s)	646 (M$^+$, 13.17)
Fe$_2$(μ-SCH$_2$Ph)(μ-SePh)(NO)$_4$	1780, 1745	7.2 (m, 10 H), 4.18 (s, 1 H), 4.10 (s, 1 H)	482 (M$^+$ − NO, 1.51)
(NO)$_4$Fe$_2$(μ_3-S)$_2$Ni(dppe)	1745	7.18 (m, 5 H), 2.35 (m, 1 H)	
(NO)$_4$Fe$_2$(μ_3-S)$_2$Pt(PPh$_3$)$_2$	1725	7.20 (m)	

^{a} CH$_2$Cl$_2$ solutions. ^{b} CDCl$_3$ solutions. ^{c} 70 ev. ^{d} P is 2% cross-linked polystyrene (see Experimental Section).

Metalation of Roussin's Red Salt: Preparation of Fe$_2$(NO)$_4$(μ_3-S)$_2$Ni(dppe). To 115 mg of K$_2$[Fe$_2$S$_2$(NO)$_4$]·8H$_2$O (0.222 mmol) in 5 mL of CH$_3$COCH$_3$ was added 118 mg of NiCl$_2$(dppe) (0.222 mmol). After it was stirred for 1 h, the reaction mixture was reduced in volume, extracted with CH$_2$Cl$_2$, and filtered through a bed of silica gel. Addition of hexane to the filtrate and cooling at −25 °C overnight gave 120 mg (73% yield) of black crystals.
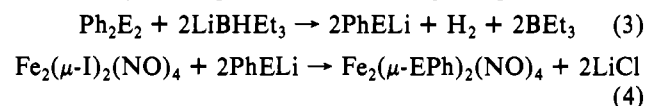
Results and Discussion

The sulfur-localized reactivity of Fe$_2$(μ-S)$_2$(NO)$_4$$^{2-}$ (**1**) was straightforwardly demonstrated by its reactions with electrophiles. Alkylation proved to be a reliable route to a variety of esters, which were easily separable from ionic impurities via silica gel chromatography. Pavel first noted that the ethyl ester Fe$_2$(μ-SEt)$_2$(NO)$_4$ could be prepared from **1** by alkylation with ethyl iodide.[17] We found that the ethyl ester prepared in this way was spectroscopically identical with that obtained by nitrosylation of ferrous ethyl mercaptide (eq 2). Other

$$Fe_2(\mu\text{-S})_2(NO)_4{}^{2-} \xrightarrow{+2EtI(-2I^-)}$$
$$Fe_2(\mu\text{-SEt})_2(NO)_4 \quad (2)$$
$$(2/n)[Fe(SEt)_2]_n \xrightarrow{+4NO(-Et_2S_2)}$$

reactive organic halides function well in this reaction, and in this way the benzyl ester and its heterogenized counterpart were prepared. The polymer-bound species, prepared from **1** and chloromethylated polystyrene, was isolated as a golden brown resin whose IR closely resembled that for the soluble analogue. This process represents an unusual version of polymer functionalization. The immobilized iron nitrosyl is of special interest since other soluble iron nitrosyls are useful olefin dimerization catalysts.[18-20] Excess 1,3-dibromopropane afforded Fe$_2$(μ-SCH$_2$CH$_2$CH$_2$Br)$_2$(NO)$_4$. This compound was identified by IR, mass spectrometry, and ^{1}H NMR spectroscopy; the latter measurement showed three multiplets of equal intensity. This ester is particularly interesting as it represents a transition-metal-stabilized derivative, the reactive mustard 3-bromopropanethiol.
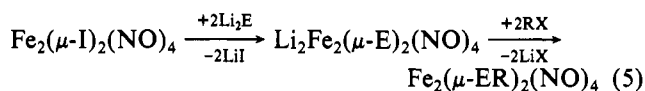
We have found that all of the Roussin esters can generally be prepared more conveniently from Fe$_2$(μ-I)$_2$(NO)$_4$ (**2**). The iodo-bridged dimer[21] recommends itself as a reagent of general inorganic synthetic value because of its availability and stability.[15] Thus treatment of **2** with 2 equiv of an organic thiol in the presence of a proton acceptor afforded good yields of the appropriate esters. We have used **2** as a precursor to the complete series of phenyl chalcogenide derivatives Fe$_2$(μ-

EPh)$_2$(NO)$_4$ (E = S, Se, Te). For the selenium and tellurium esters the synthesis proceeded in two stages (eq 3 and 4), the

$$Ph_2E_2 + 2LiBHEt_3 \rightarrow 2PhELi + H_2 + 2BEt_3 \quad (3)$$

$$Fe_2(\mu\text{-I})_2(NO)_4 + 2PhELi \rightarrow Fe_2(\mu\text{-EPh})_2(NO)_4 + 2LiCl \quad (4)$$
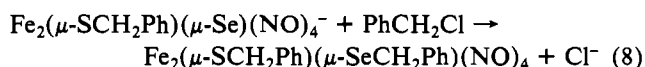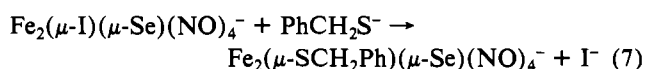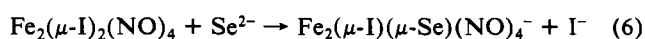
first step of which exploits the "super hydride" technology developed by Galdysz et al.[16] As a further demonstration of its general utility, **2** reacted with LiPPh$_2$ to afford Fe$_2$(μ-PPh$_2$)$_2$(NO)$_4$, whose spectroscopy matched that reported by Hayter for the same compound prepared from Fe(NO)$_2$(CO)$_2$ and Ph$_4$P$_2$.[22]

The reaction of 2 equiv of Li$_2$E (E = S, Se, Te) with **2** in THF provides a route to *anhydrous* solutions of Fe$_2$(μ-E)$_2$-(NO)$_4$$^{2-}$, which could then be alkylated. Using this methodology, we prepared esters of alkyl chalcogenides formally derived from otherwise unavailable and unstable alkylselenols and alkyltellurols (eq 5). The unstable tellurium esters proved

$$Fe_2(\mu\text{-I})_2(NO)_4 \xrightarrow[-2LiI]{+2Li_2E} Li_2Fe_2(\mu\text{-E})_2(NO)_4 \xrightarrow[-2LiX]{+2RX}$$
$$Fe_2(\mu\text{-ER})_2(NO)_4 \quad (5)$$

difficult to obtain in analytically pure form although they were unambiguously characterized by ^{1}H NMR, IR, and mass spectrometry. Generally, all of the esters reported in this paper showed an observable molecular ion peak in their mass spectra in addition to peaks attributable to sequential loss of four nitrosyl ligands.

Attempted stepwise displacement of the μ-iodo ligands of **2** by the phenyl selenide and benzyl mercaptide anions afforded a mixture of the three possible esters as ascertained by ^{1}H NMR and chromatographic comparisons with pure Fe$_2$(μ-SCH$_2$Ph)$_2$(NO)$_4$ and Fe$_2$(μ-SePh)$_2$(NO)$_4$. Column chromatography on Florisil provided a pure sample of the mixed chalcogenide ester Fe$_2$(μ-SCH$_2$Ph)(μ-SePh)(NO)$_4$. The purity of the mixed ester was established by ^{1}H NMR, TLC, and, importantly, mass spectrometry; the last technique showed weak signals for each denitrosylated ion and intense envelopes of peaks for Fe$_2$SeSCH$_2$Ph$^+$ and PhSeSCH$_2$Ph$^+$. Using similar methodology, we also prepared the analogous bis(benzyl) S–Se ester (eq 6–8), although both ^{1}H NMR and mass spectrometry indicated that this mixed chalcogenide ester contained ~10% impurity of the symmetrical dithioester Fe$_2$(μ-SCH$_2$Ph)$_2$(NO)$_4$.

$$Fe_2(\mu\text{-I})_2(NO)_4 + Se^{2-} \rightarrow Fe_2(\mu\text{-I})(\mu\text{-Se})(NO)_4{}^- + I^- \quad (6)$$

$$Fe_2(\mu\text{-I})(\mu\text{-Se})(NO)_4{}^- + PhCH_2S^- \rightarrow$$
$$Fe_2(\mu\text{-SCH}_2Ph)(\mu\text{-Se})(NO)_4{}^- + I^- \quad (7)$$

$$Fe_2(\mu\text{-SCH}_2Ph)(\mu\text{-Se})(NO)_4{}^- + PhCH_2Cl \rightarrow$$
$$Fe_2(\mu\text{-SCH}_2Ph)(\mu\text{-SeCH}_2Ph)(NO)_4 + Cl^- \quad (8)$$

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The ¹H NMR spectra of the alkyl thioesters Fe₂(μ-SEt)₂(NO)₄, Fe₂(μ-SCH₂Ph)₂(NO)₄, and Fe₂(μ-SCH₂Ph)(μ-SePh)(NO)₄ show a doubling of the alkyl signals, indicating that there exist equal quantities of the syn and anti isomers in solution. The X-ray structure of the ethyl ester revealed a planar Fe₂S₂ core with the alkyl groups disposed in the anti configuration;[5] apparently in solution both isomers coexist, and their rate of inversion is slow on the ¹H NMR time scale. In the case of the esters of Fe₂(μ-S)₂(CO)₆²⁻, the tetrahedral Fe₂S₂ core geometry gives rise to three possible geometric isomers, depending on whether the substituents occupy axial or equatorial sites on the sulfur atoms. For Fe₂(μ-SMe)₂(CO)₆, King has chromatographically separated two of these isomers.[23] Due to the long S···S distance in Fe₂(μ-SEt)₂(NO)₄ (r_{SS} = 3.63 Å[5]) compared with that for Fe₂(μ-SMe)₂(CO)₆ (r_{SS} = 2.93 Å[24]), there is little steric interaction between the organic substituents attached to the planar Fe₂S₂ core. For this reason the two isomers coexist in solution in equal populations. ¹H NMR spectroscopy revealed a splitting of the phenyl proton resonances for the PhS and PhSe esters. Since the organic chalcogenide precursors do not show this behavior, this observation is consistent with syn–anti isomerism.

syn   anti
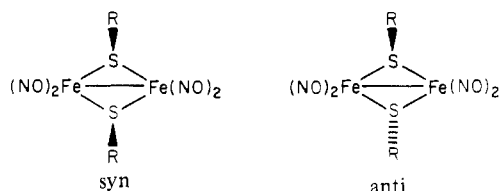
Fe₂(μ-S)₂(CO)₆²⁻ is known to undergo metalation to afford stable (CO)₆Fe₂(μ₃-S)₂MLₙ cluster compounds. We find, however, that **1** is considerably less reactive toward transition-metal electrophiles. Thus treatment of **1** with *cis*-PtCl₂(PPh₃)₂ afforded an unstable solid, which by ¹H NMR and IR contained the anticipated Fe₂S₂Pt cluster; we have previously shown that Fe₂(μ-S)₂(CO)₆²⁻ reacts with the same platinum(II) complex to afford robust (CO)₆Fe₂(μ₃-S)₂Pt(PPh₃)₂.[8,26] An unstable cluster formulated as (NO)₄Fe₂(μ₃-S)₂Ni(dppe) was isolated from the reaction of **1** and NiCl₂(dppe) (dppe = 1,2-bis(diphenylphosphino)ethane). The instability of this compound is understandable in view of the tendency of other metal complexes containing cis mercaptides to reductively eliminate their sulfur-containing ligands.[25]

Summary

In comparison with Fe₂(μ-S)₂(CO)₆²⁻, Roussin's nitrosyl anion is considerably more stable and is reactive toward a narrower range of electrophiles. These observations are consistent with the view that nitric oxide is a more effective π-acid ligand than carbon monoxide. The net result is that the nucleophilicity of metal nitrosyl complexes is attenuated relative to the analogous carbonyls. An additional finding of this study relates to the synthetic utility of Fe₂(μ-I)₂(NO)₄. This diiron reagent allows one to prepare anhydrous solutions of Fe₂(μ-E)₂(NO)₄²⁻ (E = S, Se, Te). These intermediates permit the assembly of organochalcogenide ligands in situ, thus obviating the need for noxious and unstable ligand precursors.

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Oxidation of Hydroquinone Esters and Substituted Hydroquinones by Cerium(IV) in 1 N Sulfuric Acid

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Phosphorylation of nucleophiles (N) may accompany the oxidation of hydroquinone phosphates,[1] i.e.

$$\text{(1)}$$

$$N + PO_3^- \longrightarrow NPO_3^-$$
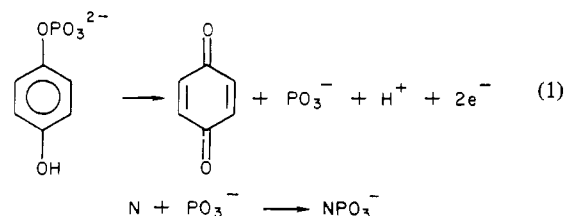
where N = H₂O, ROH, PO₄³⁻, ADP, etc.

Although P–O bond cleavage predominates in the simple hydrolysis of phosphate monoesters in their mono- and dianion forms,[2] the efficiency of oxidative phosphorylation achieved with hydroquinone phosphates typically is quite low.[1] Tracer studies with H₂¹⁸O showed that only 35% of the orthophosphate product of the reaction of Br₂ with 4-hydroxy-2,3-dimethyl-1-naphthyl dihydrogen phosphate in 1 N HClO₄ resulted from P–O bond cleavage.[3] The dominant pathway evidently involves unproductive C–O bond breaking, induced by nucleophilic displacement of H₂PO₄⁻ by water. Similarly, oxidation of hydroquinone phosphate with ceric ion in methanol gives a 95% yield of the product expected from C–O bond cleavage, the dimethyl ketal of 1,4-benzoquinone.[4]

While hydroquinone phosphates probably are not involved in biological oxidative phosphorylation, these compounds nevertheless are useful in understanding how phosphorylation may be efficiently coupled to a two-electron oxidation process. Our ultimate goal is to determine the effect of transition-metal ions on the mechanism of reactions having the potential for coupled electron and group transfer, i.e., the oxidative hydrolysis of hydroquinone esters. In this note we report kinetic studies of the oxidation of (4-hydroxyphenyl)phosphoric acid (HQ-P) and (4-hydroxyphenyl)sulfuric acid (HQ-S) by cerium(IV) in 1 N sulfuric acid. To characterize further the reactivity of Ce(IV) with phenolic substrates under these conditions, we report rate constants for the oxidation of several substituted hydroquinones (H₂Q-X). The dependence of rate on thermodynamic driving force is examined to determine whether an outer-sphere mechanism pertains in the reaction

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