Reaction of $(\mu\text{-}S)_2Fe_2(CO)_6$ dianion with 1,2-vinyl and aryl diiodides

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Dedicated to Professor Eusebio Juaristi on his 55th birthday

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Abstract

The inorganic dithiolate, $(\mu\text{-}S)_2Fe_2(CO)_6{}^{2-}$, reductively deiodinates *trans*-1,2-diiodo-1,2-diphenylethene to afford diphenylacetylene in 79% yield. Reaction of $(\mu\text{-}S)_2Fe_2(CO)_6{}^{2-}$ with 1,2-diiodobenzene and 2,3-diiodotoluene results in the formation of the benzenedithiolate complex $(\mu\text{-}S_2C_6H_4)Fe_2(CO)_6$ and toluenedithiolate complex $(\mu\text{-}S_2C_6H_4Me)Fe_2(CO)_6$ in 42% and 48% isolated yields, respectively. These reactions appear to involve reductive deiodination of 1,2-diiodobenzene and 2,3-diiodotoluene with $(\mu\text{-}S)_2Fe_2(CO)_6{}^{2-}$ to the corresponding benzynes followed by trapping with the concomitantly formed disulfide $(\mu\text{-}S_2)Fe_2(CO)_6$, to give the observed complexes. As such, these reactions involve the first examples of thermal [2+2] cycloaddition of benzyne to the S-S bond of an inorganic disulfide. Although the reaction was not observed on treatment of other substituted 1,2-diiodobenzenes, 1,2,4,5-tetraiodobenzene was monodeiodinated to 1,2,4-triiodobenzene in 62% isolated yield.

Keywords: Reductive deiodination , dinuclear iron complexes, μ-dithiolato ligands, benzyne

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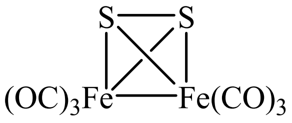
Introduction

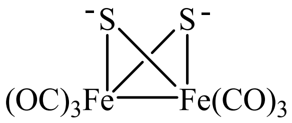
Orbital symmetry rules[1] render $[_\sigma 2_S + _\pi 2_S]$ and $[_\pi 2\ _S + _\pi 2_S]$ cycloadditions forbidden thermally but allowed photochemically. Consequently, cycloadditon of the S-S bond of dinuclear metal μ-disulfide complexes to alkenes[2] and *p*-benzoquinones[3] is promoted by light. Although benzyne undergoes thermal [2+2] cycloadditions with alkenes, symmetry rules are not violated because the reaction is not concerted. Benzyne cycloadds to *cis*- and *trans*-1,2-dichloroethenes with significant loss of stereochemistry.[4] Consequently, formation of a biradical intermediate was proposed[4] and supported by theoretical studies.[5]

Results and Discussion

Reduction of $(\mu\text{-}S_2)Fe_2(CO)_6$ **1** with $LiEt_3BH$ is known[6] to produce green dianion **2**. Alkylation of this dianion with alkyl halides is well-known[6,7] but its reaction with vinyl or aryl halides has not been previously reported. Treatment of dianion **2** with *trans*-1,2-diiodo-1,2-diphenylethene **3** provided diphenylacetylene **4** in 79% isolated yield and $(\mu\text{-}S_2)Fe_2(CO)_6$, **1,** isolated in 18% yield.



1



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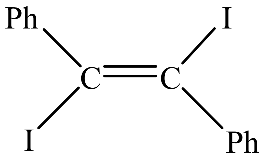

3

$PhC\equiv CPh$

4

To determine whether 1,2-diiodobenzene **5a** would undergo analogous reductive deiodo-elimination to yield benzyne the following reaction was carried out. 1,2-Diiodobenzene, **5a**, was added to a green solution of dianion **2** at -78 °C whereupon the color changed to red. After workup known complex **6a** was isolated in 42% yield after column chromatography. Complex **6a** was previously synthesized by reaction of $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$ with 1,2-benzenedithiol[8] and its crystal structure determined by X-ray methods.[9] It is presumed that dianion **2** effects deiodo-elimination of 1,2-diiodobenzene to give benzyne, analoguous to the formation of diphenylacetylene **4** from *trans*-1,2-diiodo-1,2-diphenylethene **3**. Then the disulfide **1** concomitantly formed in this reaction traps the benzyne in a [2+2] reaction to afford benzenedithiolate complex **6a**. This cycloaddition reaction does not require light and, therefore, constitutes the first example of a thermal [2+2] cycloaddition with an inorganic disulfide. As with the cycloadditions of benzyne to alkenes a stepwise mechanism avoids violation of orbital symmetry rules. Other mechanisms by which dithiolate **2** can form **6a** by reaction with **5a** can be eliminated for the following reasons. Aromatic nucleophilic substitution of unactivated aryl halides with sulfur nucleophiles is known[10] but generally requires higher temperatures. Indeed treatment of dianion **2** with iodobenzene did not give substitution products. The expected substitution products: diarylthiolato complexes $Fe_2(SAr)_2(CO)_6$, are known and synthesized by treatment of $Fe_2(CO)_9$[11] or $Na_2Fe(CO)_4$[12] with arenethiols. Aromatic nucleophilic substitution by arylthiolates by an $S_{RN}1$ mechanism is known[13] but requires photostimulation. Irradiation is not needed for the formation of **6a** from dithiolate **2** and **5a**.

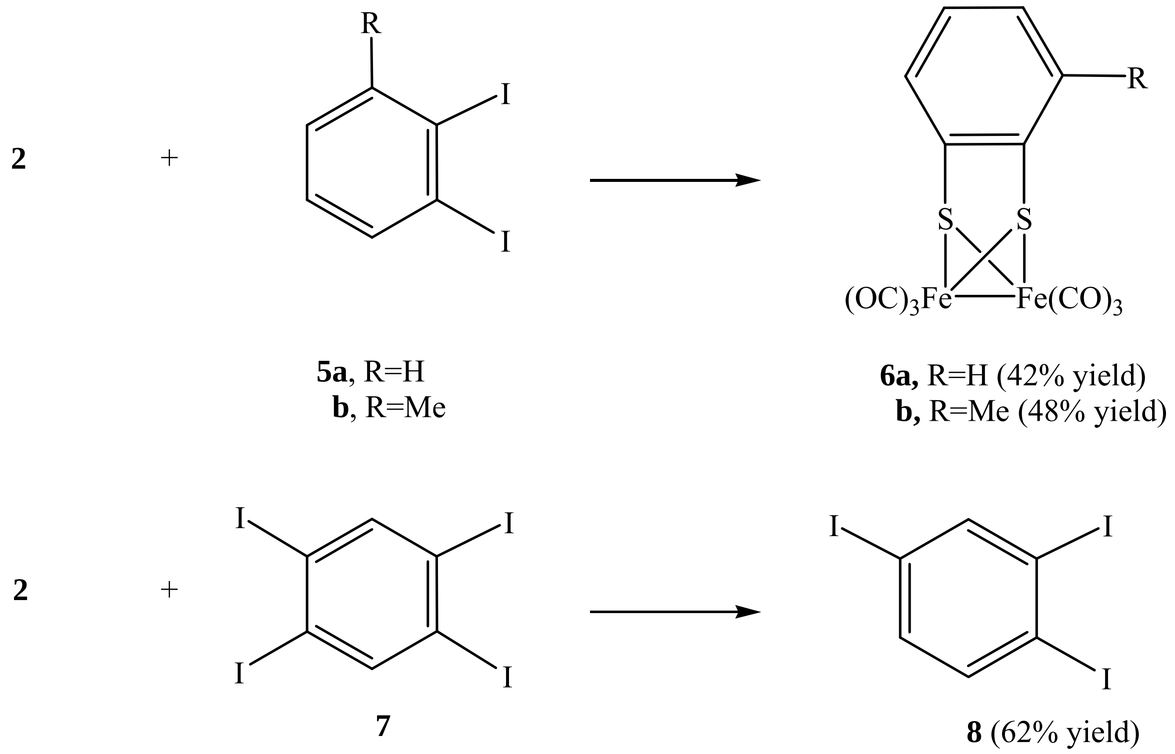

Figure 1. Reaction of dianion **2** with 1,2-diiodobenzenes.

To ascertain whether the reaction of dithiolate **2** with substituted 1,2-diiodobenzenes would provide a generally useful route to complexes **6**, variously substituted 1,2-diiodobenzenes were prepared. Reaction of 2,3-diiodotoluene **5b** with dianion **2** afforded **6b**, a previously unknown compound, in 48% yield after column chromatography. Analogous products were not formed in the reaction of **2** with 4,5-diiodo-1,2-dimethoxybenzene, 3,4-diiodonitrobenzene or 1,2,3,4-tetrafluoro-5-6-diiodobenzene nor did **6a** form using 1,2-dibromobenzene instead of **5a**. . However, 1,2,4,5-tetraiiodobenzene **7** reacted with dianion **2** to produce 1,2,4-triiodobenzene **8** in 62% yield after purification.

In conclusion, dianion **2** efficiently effects reductive deiodoelimination of **3**. Analogous reaction of aryl diiodides **5a** and **5b** is accompanied by [2+2] cycloaddition of the benzyne and disulfide formed in the reaction. Although this reaction was not successful with other aryl 1,2-diiodides and even gave reductive monodeiodination rather than elimination in the case of **7**, the reaction is the first example of an apparent thermal [2+2] cycloaddition of benzyne to an inorganic disulfide.

Experimental Section

General Procedures. All reactions were carried out under a dry, oxygen-free nitrogen atmosphere. THF was dried prior to use by distillation from sodium-benzophenone ketyl under nitrogen. The products were isolated by column chromatography over silica gel (230-400 mesh) eluting with hexanes. $(\mu\text{-}S_2)Fe_2(CO)_6$[6, 14] 2,3-diiodotoluene[15], 1,2,4,5-tetraiodobenzene[16] and trans-1,2-diiodo-1,2-diphenylethene[17] were prepared as described in the cited literature references. ^{1}H and ^{13}C NMR spectra were obtained using a Varian 300 spectrometer. The chemical shifts are reported in ppm downfield from tetramethylsilane and referenced to residual protons of $CDCl_3$ (δ =7.24). IR spectra were measured using a Nicolet Impact 410 spectrophotometer. Melting points were determined using a Büchi capillary melting point apparatus and are uncorrected. FAB MS was obtained using a JEOL HX110 mass spectrometer and GC/MS using a Varian Saturn 2000 system with a 30m x 0.22mm HP-5ms column. Elemental analyses were performed by Desert Analytics Laboratory, Tucson, AZ.

Reaction of trans-1-2-Diiodo-1,2-diphenylethene with $(\mu\text{-}S)_2Fe_2(CO)_6$ Dianion. To a stirred solution of $(\mu\text{-}S_2)Fe_2(CO)_6$ (100 mg, 0.30 mmol) in THF (4 mL) at -78 ˚C, was added $LiEt_3BH$ (0.60 mL, 1M) in THF dropwise by syringe. After completion of the addition, the dark green solution was stirred for 30 min and then a solution of trans-1,2-diiodo-1,2-diphenylethene (259 mg, 0.60 mmol) in THF (5 mL) at -78 ˚C was added with stirring. After completion of the addition the red brown solution was stirred for 1 h, allowed to warm to room temperature, stirred an additional 2 h, concentrated on a rotary evaporator and the residue chromatographed and recrystallized from hexanes to give **4** (84 mg, 79%): mp 58-60 ˚C. This material had the same IR and ^{1}H NMR spectra as authentic sample and its mixed mp with authentic sample was undepressed.

(µ-1,2-Benzenedithiolato)diiron Hexacarbonyl (6a). To a solution of dianion **2** prepared as above a solution of 1,2-diiodobenzene (99 mg, 0.30 mmol) in THF (1 mL) was added. The solution was stirred at -78 ˚C for 1 h and then allowed to warm to room temperature and stirred for 4 h. The red-brown mixture was concentrated using a rotary evaporator and the residue chromatographed to give **6a** (52 mg, 42%): mp 89-90 ˚C; ^{1}H NMR ($CDCl_3$) δ 7.84(m, 2H), 7.02(m, 2H); ^{13}C NMR($CDCl_3$) δ 107.9, 129.0, 139.3, 208.2; IR(C_6H_{14}) ν_{CO} 2079, 2044, 2004, 1998, 1960 cm^{-1}.

(µ-2,3-Toluenedithiolato)diiron Hexacarbonyl (6b). To a dianion solution prepared as above was added a solution of 2,3-diiodotoluene (206 mg, 0.60 mmol) in THF (1 mL) at -78 ˚C with stirring. After completion of the addition the solution was stirred for 1 h, allowed to warm to room temperature, stirred for an additional 3 h, concentrated on a rotary evaporator and the residue chromatographed to yield **6b** as a light red liquid (123 mg, 48%): ^{1}H NMR($CDCl_3$) δ 7.77 (d, *J* = 6.6 Hz, 1H), 7.22 (d, *J* = 6.0 Hz, 1H), 7.04 (dd, *J* = 6,6 Hz, 1H), 2.66 (s, 3H); ^{13}C NMR($CDCl_3$) δ 144.5, 137.0, 129.3, 128.4, 114.4; 109.8, 32.7; IR(neat) ν_{CO} 2079, 2039, 2007 cm^{-1}; FAB MS *m/z* 434 [M$^+$], 406 [M$^+$-CO]; HRMS *m/z* 434.0096 (calcd for $C_{13}H_6Fe_2O_6S_2$: 433.8305)

Reaction of 1,2,4,5-tetraiodobenzene with (μ-S)$_2$Fe$_2$(CO)$_6$ dianion. To a dianion solution prepared as above was added a solution of 1,2,4,5-tetraiodobenzene (175 mg, 0.30 mmol) in THF (3 mL) and pyridine (3 mL) at -78 ˚C with stirring. After completion of the addition the solution was stirred for 1 h, allowed to warm to room temperature, stirred an additional 4 h, concentrated on a rotary evaporator and the residue chromatographed and recrystallized from hexanes to give **8** (85 mg, 62%): mp 88-90 ˚C (lit.[18] 91 °C); ^{1}H NMR(CDCl$_3$) δ 8.16 (d, *J* = 2.4Hz, 1H), 7.54(d, *J* = 7.8 Hz, 1H), 7.29(dd, *J* = 8.1, 2.1Hz, 1H); ^{13}C NMR(CDCl$_3$) δ 146.8, 140.5; 138.2 109.4, 107.3; IR (CDCl$_3$) 3156, 2987, 2906, 1644, 1556, 1090 cm^{-1}; GC/MS *m/z* 456 [M$^+$]; Anal. Calcd for $C_6H_3I_3$: C, 15.79; H, 0.66%. Found: C, 16.11; H, 0.81.

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