

Reaction of $(\mu\text{-S})_2\text{Fe}_2(\text{CO})_6$ 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, $(\mu\text{-S})_2\text{Fe}_2(\text{CO})_6^{2-}$, reductively deiodinates *trans*-1,2-diiodo-1,2-diphenylethene to afford diphenylacetylene in 79% yield. Reaction of $(\mu\text{-S})_2\text{Fe}_2(\text{CO})_6^{2-}$ with 1,2-diiodobenzene and 2,3-diiidotoluene results in the formation of the benzenedithiolate complex $(\mu\text{-S}_2\text{C}_6\text{H}_4)\text{Fe}_2(\text{CO})_6$ and toluenedithiolate complex $(\mu\text{-S}_2\text{C}_6\text{H}_4\text{Me})\text{Fe}_2(\text{CO})_6$ in 42% and 48% isolated yields, respectively. These reactions appear to involve reductive deiodination of 1,2-diiodobenzene and 2,3-diiidotoluene with $(\mu\text{-S})_2\text{Fe}_2(\text{CO})_6^{2-}$ to the corresponding benzyne followed by trapping with the concomitantly formed disulfide $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$, 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.

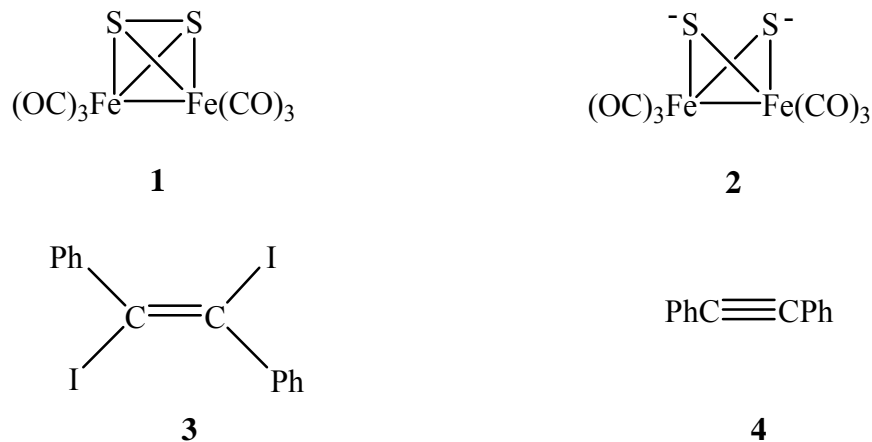
Keywords: Reductive deiodination, dinuclear iron complexes, μ -dithiolato ligands, benzyne

Introduction

Orbital symmetry rules¹ render $[\sigma_2\text{S}+\pi_2\text{S}]$ and $[\pi_2\text{S}+\pi_2\text{S}]$ cycloadditions forbidden thermally but allowed photochemically. Consequently, cycloaddition of the S-S bond of dinuclear metal μ -disulfide complexes to alkenes² and *p*-benzoquinones³ 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 proposed⁴ and supported by theoretical studies.⁵

Results and Discussion

Reduction of $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ **1** with LiEt_3BH is known⁶ 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 $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$, **1**, isolated in 18% yield.



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 $\text{Fe}_2(\text{CO})_9$ or $\text{Fe}_3(\text{CO})_{12}$ with 1,2-benzenedithiol⁸ 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, analogous 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 known¹⁰ but generally requires higher temperatures. Indeed treatment of dianion **2** with iodobenzene did not give substitution products. The expected substitution products: diarylthiolato complexes $\text{Fe}_2(\text{SAr})_2(\text{CO})_6$, are known and synthesized by treatment of $\text{Fe}_2(\text{CO})_9$ ¹¹ or $\text{Na}_2\text{Fe}(\text{CO})_4$ ¹² with arenethiols. Aromatic nucleophilic substitution by arylthiolates by an $\text{S}_{\text{RN}}1$ mechanism is known¹³ but requires photostimulation. Irradiation is not needed for the formation of **6a** from dithiolate **2** and **5a**.

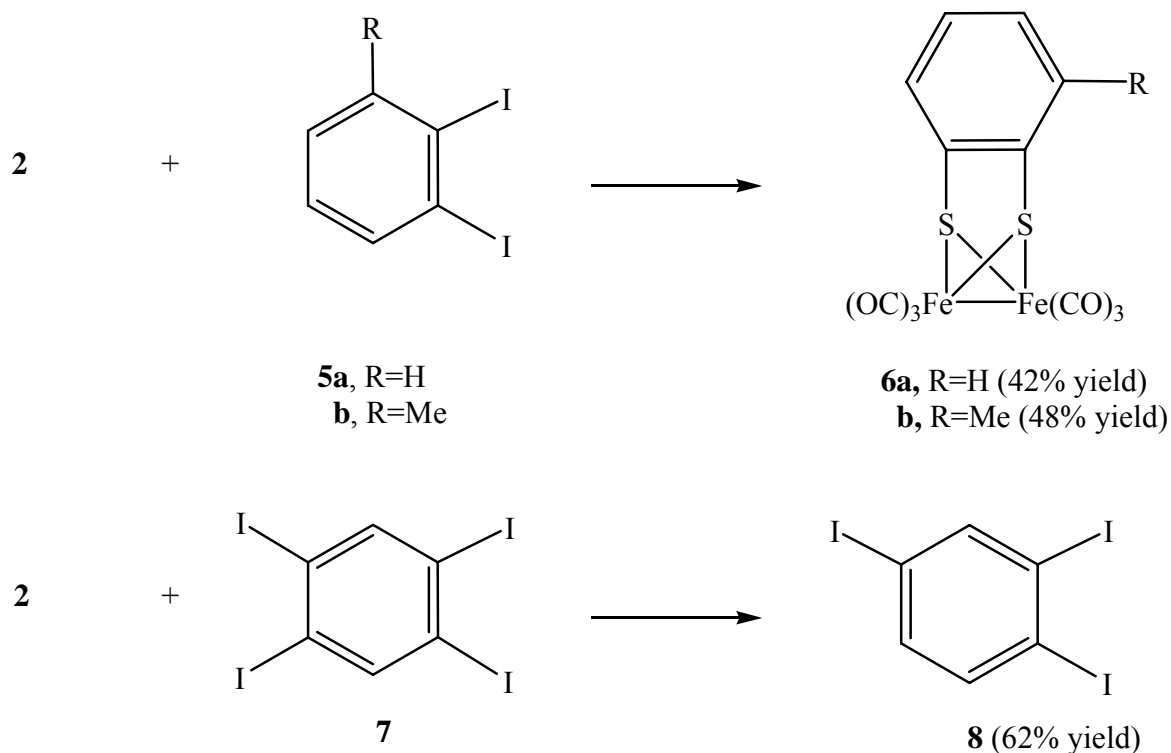


Figure 1. Reaction of dianion **2** with 1,2-diiodobenzenes.

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-tetraiodobenzene **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. $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$,^{6, 14} 2,3-diiodotoluene¹⁵, 1,2,4,5-tetraiodobenzene¹⁶ and trans-1,2-diiodo-1,2-diphenylethene¹⁷ were prepared as described in the cited literature references. ¹H and ¹³C 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 ($\delta = 7.24$). 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 $(\mu\text{-S})_2\text{Fe}_2(\text{CO})_6$ Dianion. To a stirred solution of $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ (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 $58\text{-}60^\circ\text{C}$. This material had the same IR and ¹H NMR spectra as authentic sample and its mixed mp with authentic sample was undepressed.

$(\mu\text{-1,2-Benzenedithiolato})\text{diiron Hexacarbonyl (6a)}$. 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 $89\text{-}90^\circ\text{C}$; ¹H NMR (CDCl_3) δ 7.84(m, 2H), 7.02(m, 2H); ¹³C 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} .

$(\mu\text{-2,3-Toluenedithiolato})\text{diiron Hexacarbonyl (6b)}$. 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%): ¹H 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); ¹³C 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 [$\text{M}^+ - \text{CO}$]; HRMS m/z 434.0096 (calcd for $\text{C}_{13}\text{H}_6\text{Fe}_2\text{O}_6\text{S}_2$: 433.8305)

Reaction of 1,2,4,5-tetraiodobenzene with $(\mu\text{-S})_2\text{Fe}_2(\text{CO})_6$ 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 $-78\text{ }^\circ\text{C}$ 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 $88\text{-}90\text{ }^\circ\text{C}$ (lit.¹⁸ $91\text{ }^\circ\text{C}$); ^1H NMR(CDCl_3) δ 8.16 (d, $J = 2.4\text{ Hz}$, 1H), 7.54(d, $J = 7.8\text{ Hz}$, 1H), 7.29(dd, $J = 8.1, 2.1\text{ Hz}$, 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 $\text{C}_6\text{H}_3\text{I}_3$: C, 15.79; H, 0.66%. Found: C, 16.11; H, 0.81.

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