Reaction of (µ-S)2Fe2(CO)6 dianion with 1,2-vinyl and aryl diiodides

Richard S. Glass* and Maya S. Singh†

Department of Chemistry, The University of Arizona, Tucson, AZ  85721, U.S.A.
† On leave from DDU Gorakhpur University, Gorakhpur, India
E-mail: rglass@u.arizona.edu

Dedicated to Professor Eusebio Juaristi on his 55th birthday
(received 24 Mar 05; accepted 03 May 05; published on the web 05 May 05)

Abstract
The inorganic dithiolate, (µ-S)2Fe2(CO)62-, reductively deiodinates trans-1,2-diiodo-1,2-diphenylethene to afford diphenylacetylene in 79% yield. Reaction of (µ-S)2Fe2(CO)62- with 1,2-diiodobenzene and 2,3-diiodotoluene results in the formation of the benzenedithiolate complex (µ-S2C6H4)Fe2(CO)6 and toluenedithiolate complex (µ-S2C6H4Me)Fe2(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 (µ-S)2Fe2(CO)62- to the corresponding benzyne followed by trapping with the concomitantly formed disulfide (µ-S2)Fe2(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 rules render [σ2s+π2s] and [π2s+π2s] cycloadditions forbidden thermally but allowed photochemically. Consequently, cycloaddition of the S-S bond of dinuclear metal µ-disulfide complexes to alkenes and p-benzoquinones 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. Consequently, formation of a biradical intermediate was proposed and supported by theoretical studies.
Results and Discussion

Reduction of \((\mu-S_2)Fe_2(CO)_6\) 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 \((\mu-S_2)Fe_2(CO)_6\) 1, isolated in 18\% yield.

![Chemical Structures]

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, 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 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\(_{RN1}\) mechanism is known\(^13\) but requires photostimulation. Irradiation is not needed for the formation of 6a from dithiolate 2 and 5a.
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-diiiodonitrobenzene 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.

Figure 1. Reaction of dianion 2 with 1,2-diiodobenzenes.
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. \((\mu-S_2)Fe_2(CO)_6\)\(^6\), \(^{14}\) 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\(_3\) (\(\delta = 7.24\)). 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 \((\mu-S_2)Fe_2(CO)_6\) Dianion. To a stirred solution of \((\mu-S_2)Fe_2(CO)_6\) (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.

\((\mu-1,2-Benzenedithiolato)diiron Hexacarbonyl (6a).\) 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\(_3\)) \(\delta\) 7.84(m, 2H), 7.02(m, 2H); \(^13\)C NMR(CDCl\(_3\)) \(\delta\) 107.9, 129.0, 139.3, 208.2; IR(C\(_6\)H\(_{14}\)) \(\nu\)CO 2079, 2044, 2004, 1998, 1960 cm\(^{-1}\).

\((\mu-2,3-Toluenedithiolato)diiron Hexacarbonyl (6b).\) 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\(_3\)) \(\delta\) 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\(_3\)) \(\delta\) 144.5, 137.0, 129.3, 128.4, 114.4; 109.8, 32.7; IR(neat) \(\nu\)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$_6$Fe$_2$O$_6$S$_2$: 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. 1891 °C); $^1$H NMR(CDCl$_3$) $\delta$ 8.16 (d, $J = 2.4$ Hz, 1H), 7.54 (d, $J = 7.8$ Hz, 1H), 7.29 (dd, $J = 8.1, 2.1$ Hz, 1H); $^{13}$C NMR(CDCl$_3$) $\delta$ 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$_6$H$_3$I$_3$: C, 15.79; H, 0.66%. Found: C, 16.11; H, 0.81.

**Acknowledgments**

Acknowledgment is made to the Donors of The Petroleum Research Fund, administered by the American Chemical Society for support of this research.

**References and Footnotes**