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# Synthesis of (1*Z*,3*Z*)-1,4-dibromobutadiene, (1*Z*,3*Z*)-1-bromo-4-lithiobutadiene and (1*Z*,3*Z*)-1,4-dilithiobutadiene; structure of (1*Z*,3*Z*)-($\eta^5$-$C_5H_5$)Fe(CO)$_2$CH=CHCH=CHBr

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## Abstract

An expedient synthesis of previously unknown (1Z,3Z)-1,4-dibromobutadiene is reported. When this dibromide is treated with s- or t-butyllithium, (1Z,3Z)-1-bromo-4-lithio-butadiene is generated. Treatment of the dibromide with four equivalents of t-butyllithium gives (1Z,3Z)-dilithiobutadiene. Reaction of (1Z,3Z)-1-bromo-4-lithiobutadiene with ($\eta^5$-$C_5H_5$)Fe(CO)$_2$I gives (1Z,3Z)-($\eta^5$-$C_5H_5$)Fe(CO)$_2$CH=CHCH=CHBr. X-ray crystallographic analysis of this latter compound establishes the geometry about the bromobutadiene ligand.

## Introduction

The synthesis of dihalobutadienes and their metallation reactions are of wide interest. Recently Ashe and Drone reported the stereoselective synthesis of (1Z,3Z)-1,4-diiodobutadiene [1]. Its lithium-halogen exchange reaction gave the previously unknown 1,4-dilithiobutadiene. 1,4-Dilithiobutadiene is of interest to theoretical chemists [2] and is useful for the preparation of unsubstituted five membered heterocyclic compounds [1]. We here report a one pot conversion of (1*E*,3*E*)-bis(trimethylsilyl)butadiene (**1**) [3 *] to previously unknown (1Z,3Z)-1,4-dibromobutadiene (**2**), and the mono- and di-lithium-bromine exchange reactions of **2** with alkyllithium reagents. The monolithium–halogen exchange reaction product was utilized to prepare (1Z,3Z)-($\eta^5$-$C_5H_5$)Fe(CO)$_2$CH=CHCH=CHBr (**4**), whose stereochemistry was verified by an X-ray crystallographic determination. These

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* A reference number with an asterisk indicates a note in the list of references.

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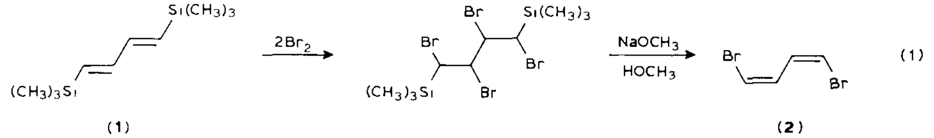
reactions can be carried out in moderate to large scale thus making available reasonable quantities of the 1,4-dibromobutadiene and its exchange products.

## Results and discussion

Dibromobutadiene **2** was prepared from **1** by bromination followed by desilylbromination with sodium methoxide in methanol (eq. 1) [4]. The crude product which can be partially purified by vacuum transfer was suitable for use in the lithium–halogen exchange reactions described below. Further purification, however, can be accomplished by column chromatography on silica gel. The dibromide **2** is a thermally sensitive oil which should only be stored for short times at cold temperatures. Its $^1H$ NMR spectrum exhibits an AA′BB′ pattern with multiplets centered at $\delta$ 5.9 and 6.7 ppm. The $^{13}C$ NMR spectrum has two absorptions appearing at 112 and 128 ppm.



Monolithium exchange reactions of **2** were attempted with three different alkyllithium reagents commonly used to affect this type of transformation. When **2** in ethyl ether or THF is treated with n-butyllithium at temperatures ranging from −78 °C to room temperature a black polymeric product is obtained. However, introduction of a cold ether solution of **2** to either one equivalent of s-butyllithium or two equivalents of t-butyllithium [5] results in exchange of one bromine to give **3**. When this solution is treated with $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ followed by chromatography, a brown solid identified as **4** is isolated (eq. 2). The $^1H$ NMR of **4** gives a single cyclopentadienyl resonance indicative of a single isomer being present. Red-brown crystals of **4** can be obtained from pentane. These crystals were analyzed by X-ray crystallographic techniques. Figure 1 shows an ORTEP diagram where the 1*Z*,3*Z* geometry of the butadiene moiety is clearly defined. Thus monolithium–bromine

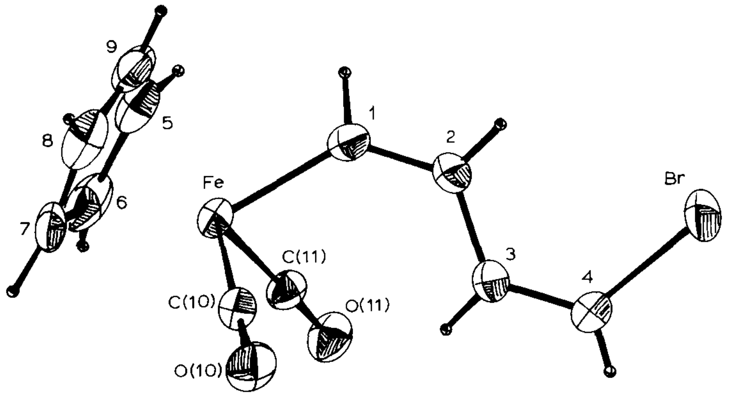
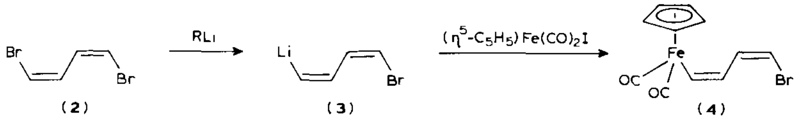


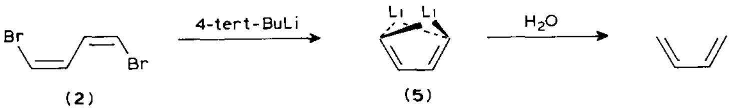
Fig. 1. ORTEP of $(1Z,3Z)\text{-}(\eta^5\text{-}C_5H_5)Fe(CO)_2CH{=}CHCH{=}CHBr$ (**4**).

exchange of **2** as well as the subsequent coupling reaction with iron occurred with retention of configuration about the vinyl carbon–bromine bond.



(2)

Work regarding the exchange of both halogens has been limited to treatment of **2** at low temperature with four equivalents of t-butyllithium. When this reaction mixture was quenched with water, butadiene is observed (gas chromatographic analysis) indicating exchange of both bromines to give **5** (eq. 3).



(3)

## Experimental

All melting points were obtained on a Thomas Hoover melting point apparatus and are uncorrected. Nuclear magnetic resonance spectra were obtained on either a Varian EM-360 spectrometer operating at 60 MHz ($^1H$) or a Jeol FX90Q spectrometer operating at 90 MHz ($^1H$) or 22.5 MHz ($^{13}C$). Chemical shifts are expressed in parts per million (ppm) downfield from tetramethylsilane which was used as an internal standard. Infrared spectra were obtained on a Perkin–Elmer Model 283 infrared recording spectrometer. Mass spectra were obtained on a Kratos MS 50 spectrometer.

Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. Diethyl ether and tetrahydrofuran were refluxed under nitrogen over sodium and benzophenone and distilled immediately prior to use. Pentane was stirred over $H_2SO_4$, washed with water, saturated $NaHCO_3$, and then water. After drying with magnesium sulfate it was distilled from $P_2O_5$ and stored under nitrogen. Nitrogen gas was passed through a column of BASF catalyst to remove residual oxygen, and then through a calcium sulfate drying column into an all glass and metal dual manifold nitrogen/vacuum line.

### *(1Z,3Z)-1,4-Dibromobutadiene (2)*

A 100 ml round bottom flask fitted with septum, magnetic stir bar, nitrogen inlet and ice bath was charged with 1.59 g (8 mmol) bis(trimethylsilylbutadiene) (1) [3] and 50 ml of purified pentane. After purging with nitrogen, 0.82 g (16 mmol) bromine in 5 ml pentane was added dropwise. The reaction mixture was stirred at this temperature for ca. 5 minutes where the solvent was then removed on the rotary evaporator. Immediately upon concentration of the products, 80 mmol of sodium methoxide in 30 ml cold (ice bath) methanol was added all at once. After stirring for 3 h, 250 ml ethyl ether was added and the solution washed 9 times with 125 ml water. The organic layer was then dried with magnesium sulfate and the solvent was removed on the rotary evaporator. Vacuum transfer (25 °C, 0.1 mmHg) to a cold trap (ice bath) gives 0.97 g (57%) of the product which is of sufficient purity for further reactions. To obtain higher purity after vacuum transfer, this product can be chromatographed on a 2.5 cm by 150 cm silica gel column with 1% fluorescent indicator (quartz glass column) and eluting with pentane. The title compound elutes in the first half of the first band as indicated by a 254 nm UV lamp. $^1$H NMR ($C_6D_6$): $\delta$ 5.9 (m, 2H, HCBr), 6.7 (m, 2H, HC) ppm; $^{13}$C NMR (22.6 MHz, $CDCl_3$): 112, 128 ppm; IR (neat): 3080m, 3025w, 1680w, 1550s, 1330w, 1290s, 825m, 680s cm$^{-1}$; mass spectrum: $m/z$ ($M^+$) calcd. for $C_4H_4Br_2$ 213.864, 211.866, 209.868, obsd. 213.863, 211.864, 209.867.

### *(1Z,3Z)-1-Bromo-4-lithiobutadiene (**3**); (1Z,3Z)-1-Cyclopentadienyl(dicarbonyliron)-4-bromobutadiene (**4**)*

An ether solution (30 ml) of **2** (1.21 g, 5.7 mmol) was cooled in a dry ice/2-propanol bath. To this solution s-butyllithium (5.2 ml, 5.7 mmol, 1.3 *M* in cyclohexane) was added dropwise via a syringe. On gradual warming (30 minutes) to − 20 ° C the yellow mixture became brown. This was stirred for an additional thirty minutes, cooled in a dry ice/2-propanol bath, and used immediately.

An ethyl ether solution (50 ml) of cyclopentadienyldicarbonyliron iodide [6] (1.54 g, 4.13 mmol) was then added dropwise to the above solution via cannula over five minutes. After stirring for 2 h the reaction mixture was warmed to room temperature, 5 g of alumina added, and the solvent removed in vacuo. This coated alumina was transferred to the top of a 2.5 cm diameter column of neutral alumina (30 g, activity grade III). Rapid chromatography with pentane as the eluent, collection of the first yellow band, and removal of pentane gave 0.290 g (23%) of a brown solid identified as **4**. Red-brown needles, m.p. 75–78 ° C, can be obtained by slow evaporation of pentane. $^1$H NMR (60 MHz, $C_6D_6$): $\delta$ 4.0 (s, 5H, $C_5H_5$), 5.9–7.8 (m, 4H, $C_4H_4Br$); IR: $\mu$(CO) 2000, 1970 cm$^{-1}$.

### *(1Z,3Z)-1,4-Dilithiobutadiene (**5**)*

An ether solution (10 ml) of **2** (0.159 g, 0.75 mmol) was cooled (dry ice/2-pro-

Table 1

Fractional atomic coordinates, thermal parameters, and their esd's for ($\eta^5$-$C_5H_5$)Fe(CO)$_2$CH=CHCH=CHBr

| Atom | $x$ | $y$ | $z$ | $B_{eq}$ (Å$^2$) |
|---|---|---|---|---|
| Br | 0.32516(5) | 0.85507(5) | 0.34294(4) | 5.734(8) |
| Fe | 0.80553(5) | 0.29255(5) | 0.22886(4) | 2.749(7) |
| O(10) | 0.8813(4) | 0.6132(3) | 0.0899(3) | 5.19(6) |
| O(11) | 0.4204(3) | 0.1669(3) | 0.0847(3) | 4.84(6) |
| C(1) | 0.7091(5) | 0.4346(4) | 0.3493(3) | 3.82(7) |
| C(2) | 0.5909(4) | 0.5535(4) | 0.3354(3) | 3.63(6) |
| C(3) | 0.4902(4) | 0.6118(4) | 0.2165(3) | 3.30(6) |
| C(4) | 0.3754(5) | 0.7302(5) | 0.2034(3) | 3.92(7) |
| C(5) | 0.8580(5) | 0.0651(5) | 0.3326(4) | 5.04(8) |
| C(6) | 0.8725(5) | 0.0378(5) | 0.2085(4) | 6.16(9) |
| C(7) | 1.0206(5) | 0.1736(6) | 0.1864(4) | 7.54(8) |
| C(8) | 1.0902(5) | 0.2787(5) | 0.3075(5) | 5.55(9) |
| C(9) | 0.9914(5) | 0.2080(5) | 0.3894(4) | 5.13(8) |
| C(10) | 0.8498(4) | 0.4865(4) | 0.1442(3) | 3.47(6) |
| C(11) | 0.5717(4) | 0.2173(4) | 0.1416(3) | 3.28(6) |

Table 2

Selected distances (Å) and angles (°) for ($\eta^5$-$C_5H_5$)Fe$(CO)_2$-CH=CHCH=CHBr

| | | | |
|---|---|---|---|
| Fe–C(10) | 1.749(3) | C(10)–Fe–C(11) | 96.8(1) |
| Fe–C(11) | 1.750(3) | C(10)–Fe–C(1) | 89.5(1) |
| Fe–C(1) | 1.971(3) | C(11)–Fe–C(1) | 88.2(1) |
| Fe–C(Cp) ave | 2.09(2) | Fe–C(1)–C(2) | 135.0(2) |
| C(1)–C(2) | 1.341(4) | C(1)–C(2)–C(3) | 127.2(3) |
| C(2)–C(3) | 1.426(4) | C(2)–C(3)–C(4) | 127.0(3) |
| C(3)–C(4) | 1.320(4) | C(3)–C(4)–Br | 124.2(2) |
| C(4)–Br | 1.871(3) | Fe–C(10)–O(10) | 179.0(3) |
| C(10)–O(10) | 1.140(3) | Fe–C(11)–O(11) | 179.3(2) |
| C(11)–O(11) | 1.135(3) | C–C–C(Cp) ave | 108(4) |
| C–C(Cp) ave | 1.37(5) | | |

panol bath) under a nitrogen atmosphere. tert-Butyllithium (0.83 ml, 1.5 mmol. 1.5 *M* in pentane) was added slowly down the side of the flask. The solution was warmed to 0 °C. During warm up the yellow solution changed to brown. After cooling again to −78 °C, a solution of ethyl ether/water was added. Upon warming to room temperature, gas chromatographic analysis of the solution was performed. Two low boiling components (other than solvent) were identified. Peak matching with standard samples indicate butadiene and 2-methylpropane were present.

*X-ray crystallographic analysis of **4***

Crystals of **4** obtained from pentane solutions by slow evaporation. $C_{11}H_9FeO_2Br$, FW = 309.0, triclinic, $P1$, $a$ 7.402(3), $b$ 7.499(2), $c$ 10.574(7) Å, $\alpha$ 91.41(4), $\beta$ 103.42(4), $\gamma$ 99.97(2)°, $V$ 561.0(9) Å, $Z = 2$, $D_x$ 1.83 g cm$^{-3}$, $\lambda$(Mo-$K_\alpha$) 0.71073 Å, $\mu$ 48.5 cm$^{-1}$, $F(000) = 304$ and $T$ 293 K. Intensities measured with an Enraf–Nonius CAD-4 diffractometer using variable speed (3 to 17 deg/min) $\omega$–$2\theta$ scans. Unit cell determined from least-squares of angle data for 25 reflections with $20° < 2\theta < 28°$. Absorption correction based on $\psi$ scans varied from 0.84 to 1.00. Data collected to $\sin\theta/\lambda$ of 0.60, $-8 \le h \le 8$, $-8 \le k \le 18$, $0 \le l \le 12$. Three standard reflections (3–32, −2–33, 24–3) varied < 2% during data collection. 2709 reflections measured, 2569 unique ($R_{int} = 0.03$), 2232 reflections with $I > 3\sigma(I)$ considered observed. Solved by MULTAN and Fourier methods. Full-matrix least-squares minimized $\Sigma w(\Delta F)^2$.

Non-H atoms were refined anisotropically; H atoms (except H(7)) were refined with constrained isotropic $B$ values of 5.0 Å$^2$, for a total of 160 variables. $R = 0.032$, $R_w = 0.040$, and $S = 1.42$ where non-Poisson $w^{-1} = (\sigma^2(I) + 0.0036I^2)/4F^2$. Final $(\Delta/\sigma)_{max} < 0.01$ and $\Delta\rho_{max} = 0.35(4)$ e$^-$ Å$^{-3}$ on final difference map. Atomic scattering factors and anomalous dispersion corrections from International Tables for X-ray Crystallography (1974) and programs used were those of the Enraf–Nonius (1982) SDP package. Table 1 gives atom coordinates and isotropic equivalent thermal parameters. Table 2 gives selected bond distances and angles.

## Acknowledgement

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