

## The Variety of Compounds from the Reaction of *ortho*-Bis(trimethylsilylethynyl)benzene with Iron Nonacarbonyl

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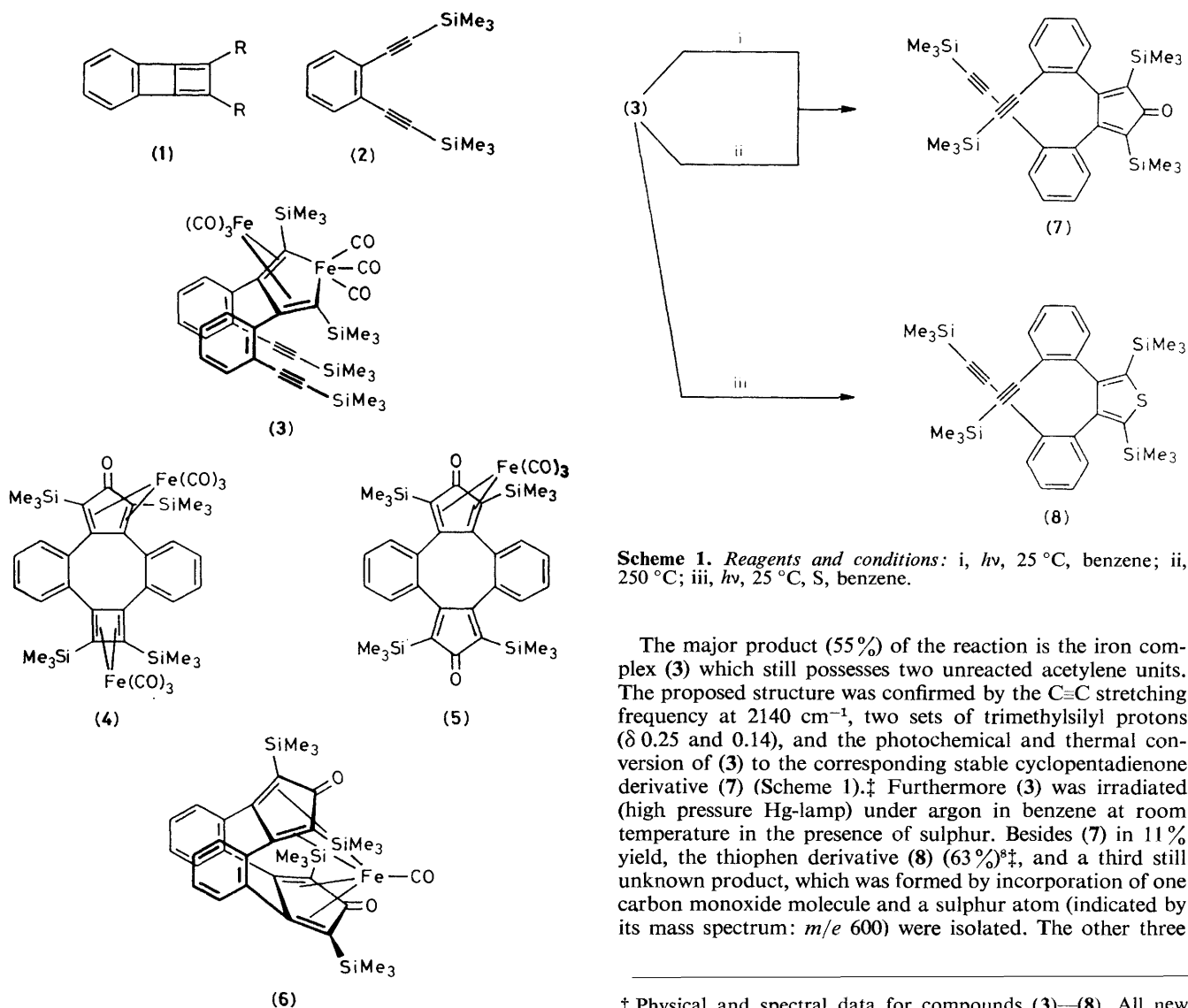
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The reaction of *ortho*-bis(trimethylsilylethynyl)benzene with iron nonacarbonyl yields a number of transition metal complexes bearing novel ligands and a new type of transition metal complex.

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Recently, *o*-bis(ethynyl)benzene derivatives<sup>1</sup> have been valuable reagents for organic synthesis, *e.g.* of verdene<sup>2</sup> and indenoindenes.<sup>3</sup> The question, however, of interactions in the

co-ordination sphere of transition metals has been somewhat neglected,<sup>3,4</sup> although a number of interesting and novel species could be expected. We aimed to synthesise the cyclo-



**Scheme 1.** Reagents and conditions: i,  $h\nu$ , 25 °C, benzene; ii, 250 °C; iii,  $h\nu$ , 25 °C, S, benzene.

The major product (55%) of the reaction is the iron complex (3) which still possesses two unreacted acetylene units. The proposed structure was confirmed by the  $\text{C}\equiv\text{C}$  stretching frequency at  $2140\text{ cm}^{-1}$ , two sets of trimethylsilyl protons ( $\delta$  0.25 and 0.14), and the photochemical and thermal conversion of (3) to the corresponding stable cyclopentadienone derivative (7) (Scheme 1).<sup>‡</sup> Furthermore (3) was irradiated (high pressure Hg-lamp) under argon in benzene at room temperature in the presence of sulphur. Besides (7) in 11% yield, the thiophen derivative (8) (63%)<sup>‡</sup>, and a third still unknown product, which was formed by incorporation of one carbon monoxide molecule and a sulphur atom (indicated by its mass spectrum:  $m/e$  600) were isolated. The other three

butadiene system (1), which might be stabilized by mesomeric and steric effects, by use of the reactions of *o*-bis(ethynyl)benzene derivatives with transition metal complexes. Such a process appeared likely since *o*-bis(phenylethynyl)benzene *per se* exhibits intramolecular interaction between the triple bonds on reaction with electrophilic, nucleophilic, or radical reagents.<sup>5,6</sup>

However, reaction of *o*-bis(trimethylsilyl)ethynylbenzene (2)<sup>†</sup> with iron nonacarbonyl in refluxing benzene did not yield the desired complex of (1). Instead, a variety of deeply coloured, crystalline iron complexes bearing novel ligands of theoretical interest were formed in excellent yield (85–95%). Product separation was achieved by column chromatography on silica-gel with benzene and acetone as eluants. The structures were assigned from their spectroscopic data.

<sup>†</sup> Compound (2) was synthesised from *o*-bis(ethynyl)benzene<sup>7</sup> by trimethylsilylation: 88%, colourless needles, m.p. 50.0–50.5 °C (from hexane); <sup>1</sup>H-n.m.r. (<sup>2</sup>H<sub>6</sub>acetone)  $\delta$  7.63–7.30 (4H, m), and 0.30 (18H, s); i.r. (CCl<sub>4</sub>)  $\nu$  3060w, 2960s, 2900m, 2160s, 1475m, 1440m, and 1249s  $\text{cm}^{-1}$ ; mass spectrum  $m/e$  270 ( $M^+$ , 17%), 255(36%), and 73(100%).

<sup>‡</sup> Physical and spectral data for compounds (3)–(8). All new compounds gave satisfactory C and H analytical and/or high resolution mass spectral data. (3): 55%; m.p. 181 °C (dec.); i.r. (KBr)  $\nu$  2140m (C=C), 2060, 2015, 1995, 1975, 1912s (Fe–CO), and 1248s (Me<sub>3</sub>Si)  $\text{cm}^{-1}$ ; mass spectrum (relative intensity)  $m/e$  820(2,  $M^+$ ), 792(9,  $M^+ - \text{CO}$ ), 708(50), 680(48), 652(96), 624(25), and 73(62, Me<sub>3</sub>Si); <sup>1</sup>H-n.m.r. (<sup>2</sup>H<sub>6</sub>acetone)  $\delta$  7.47–7.27 (4H, m), 7.27–7.06 (4H, m), 0.25 (18H, s), and 0.14 (18H, s). (4): 6%; m.p. 173 °C (dec.); i.r. (KBr)  $\nu$  2040, 1980, 1935s (Fe–CO), 1645s (CO), and 1245s (Me<sub>3</sub>Si)  $\text{cm}^{-1}$ ;  $m/e$  848(1,  $M^+$ ), 820(1,  $M^+ - \text{CO}$ ), 792(2,  $M^+ - 2\text{CO}$ ), 764(4), 736(9), 708(10), 680(18), 652(58), 624(25), 596(5), and 73(100, Me<sub>3</sub>Si); <sup>1</sup>H-n.m.r. (<sup>2</sup>H<sub>6</sub>benzene)  $\delta$  6.73 (8H, br. s.), 0.30 (18H, s), and 0.07 (18H, s). (5): 18%; m.p. 232 °C (dec.); i.r. (CHCl<sub>3</sub>)  $\nu$  2080, 2015, 2000s (Fe–CO), 1680s (CO), 1620s (CO), and 1250s (Me<sub>3</sub>Si)  $\text{cm}^{-1}$ ;  $m/e$  736(2,  $M^+$ ), 708(3,  $M^+ - \text{CO}$ ), 680(22), 652(100), 580(14), and 73(52, Me<sub>3</sub>Si); <sup>1</sup>H-n.m.r. (<sup>2</sup>H<sub>6</sub>acetone)  $\delta$  7.90–7.53 (8H, m), 0.30 (18H, s), and 0.13 (18H, s). (6): 4%; m.p. 268 °C (dec.); i.r. (KBr)  $\nu$  2040s (Fe–CO); 1635s (CO), and 1250s (Me<sub>3</sub>Si)  $\text{cm}^{-1}$ ;  $m/e$  680(14,  $M^+$ ), 652(100,  $M^+ - \text{CO}$ ), and 73(18, Me<sub>3</sub>Si); <sup>1</sup>H-n.m.r. (<sup>2</sup>H<sub>6</sub>acetone)  $\delta$  7.37 (8H, br. s.), and 0.07 (36H, s). (7): 58% from photolytic and 45% from thermal decomposition of complex (3); m.p. 155 °C (from ether–pentane); i.r. (CHCl<sub>3</sub>)  $\nu$  2960s, 2930m, 2900m, 2160s (C=C), 1690s (CO), and 1250s (Me<sub>3</sub>Si)  $\text{cm}^{-1}$ ;  $m/e$  568(4,  $M^+$ ), 553(9,  $M^+ - \text{Me}$ ), 495(9,  $M^+ - \text{Me}_3\text{Si}$ ), 480(7), and 73(100, Me<sub>3</sub>Si); <sup>1</sup>H-n.m.r. (<sup>2</sup>H<sub>6</sub>acetone)  $\delta$  7.57–7.13 (8H, m), 0.33 (18H, s), and 0.04 (18H, s). (8): 63%; m.p. 136 °C (from hexane–acetone); i.r. (CHCl<sub>3</sub>)  $\nu$  2960s, 2930s, 2900s, 2160s (C=C), 1490m, 1440m, and 1250s (Me<sub>3</sub>Si)  $\text{cm}^{-1}$ ;  $m/e$  572(6,  $M^+$ ), 557(1,  $M^+ - \text{Me}$ ), 499(16,  $M^+ - \text{Me}_3\text{Si}$ ), 484(22), 469(11), 411(38), 381(10), and 73(100, Me<sub>3</sub>Si); <sup>1</sup>H-n.m.r. (<sup>2</sup>H<sub>6</sub>acetone)  $\delta$  7.29–7.15 (8H, m), 0.10 (18H, s), and 0.08 (18H, s).

compounds (4)—(6) represent interesting complexes bearing novel organic ligands of theoretical interest. Structural assignments rest on mass spectra which reveal the basic composition, on  $^1\text{H}$ -n.m.r. data which indicate the symmetry of the structures (particularly by the number of trimethylsilyl peaks), and on the characteristic i.r. absorptions. Structural characterisation of a fifth iron complex, however, was not possible by physical or chemical methods; an *X*-ray study of this species is under investigation.

Compounds (4)—(6) represent reactive bimolecular condensation products of the diyne (2) in which molecular stabilisation is achieved through the interaction of the cyclobutadiene and cyclopentadienone ring systems with the  $\text{Fe}(\text{CO})_5$  fragment in (4) and (5) and by  $\text{Fe}(\text{CO})$ -cyclopentadienone complexation in (6); a new example of the equivalence of  $\text{Fe}(\text{CO})_5$ ,  $\text{Fe}(\text{CO})(\text{cyclobutadiene})$ ,<sup>8</sup> and  $\text{Fe}(\text{CO})(\text{cyclopentadienone})$  groups. One cyclopentadienone unit in (5) remains uncomplexed; another example of the stable monomeric 2,5-bis(trimethylsilyl)cyclopentadienones described earlier.<sup>9</sup>

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