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

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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.

Recently, *o*-bis(ethynyl)benzene derivatives[1] have been valuable reagents for organic synthesis, *e.g.* of verdene[2] and indenoindenes.[3] The question, however, of interactions in the co-ordination sphere of transition metals has been somewhat neglected,[3,4] although a number of interesting and novel species could be expected. We aimed to synthesise the cyclo-

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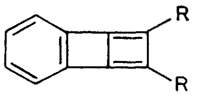
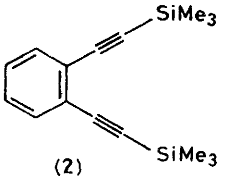


(1)



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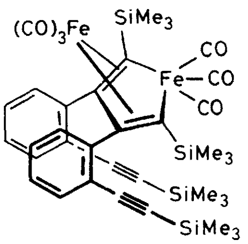

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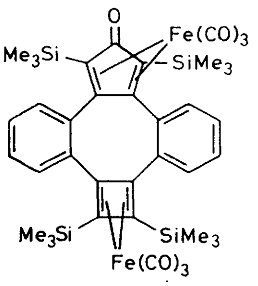

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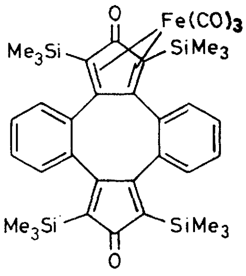

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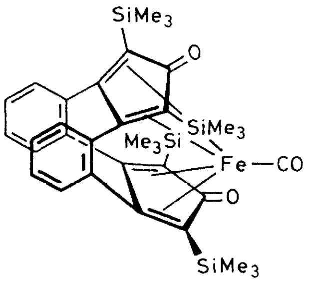
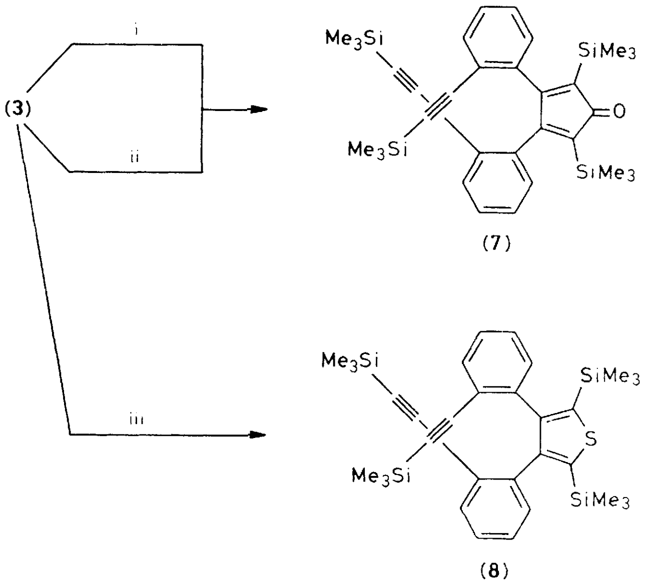


(6)

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.[5,6]

However, reaction of *o*-bis(trimethylsilylethynyl)benzene (**2**)† 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.



Scheme 1. *Reagents and conditions:* i, *h*ν, 25 °C, benzene; ii, 250 °C; iii, *h*ν, 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 C≡C stretching frequency at 2140 cm^{-1}, two sets of trimethylsilyl protons (δ 0.25 and 0.14), and the photochemical and thermal conversion of (**3**) to the corresponding stable cyclopentadienone derivative (**7**) (Scheme 1).‡ 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%)[8]‡, 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

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† Compound (**2**) was synthesised from *o*-bis(ethynyl)benzene[7] by trimethylsilylation: 88%, colourless needles, m.p. 50.0—50.5 °C (from hexane); ^{1}H-n.m.r. ([^{2}H$_6$]acetone) δ 7.63—7.30 (4H, m), and 0.30 (18H, s); i.r. (CCl$_4$) ν 3060w, 2960s, 2900m, 2160s, 1475m, 1440m, and 1249s cm^{-1}; mass spectrum *m/e* 270 (*M*$^+$, 17%), 255(36%), and 73(100%).

‡ 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) ν 2140m (C≡C), 2060, 2015, 1995, 1975, 1912s (Fe–CO), and 1248s (Me$_3$Si) cm^{-1}; mass spectrum (relative intensity) *m/e* 820(2, *M*$^+$), 792(9, *M*$^+$ – CO), 708(50), 680(48), 652(96), 624(25), and 73(62, Me$_3$Si); ^{1}H-n.m.r. ([^{2}H$_6$]acetone) δ 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) ν 2040, 1980, 1935s (Fe–CO), 1645s (CO), and 1245s (Me$_3$Si) cm^{-1}; *m/e* 848 (1, *M*$^+$), 820 (1, *M*$^+$ – CO), 792 (2, *M*$^+$ – 2CO), 764(4), 736(9), 708(10), 680(18), 652(58), 624(25), 596(5), and 73(100, Me$_3$Si); ^{1}H-n.m.r. ([^{2}H$_6$]benzene) δ 6.73 (8H, br. s,), 0.30 (18H, s), and 0.07 (18H, s). (**5**): 18%; m.p. 232 °C (dec.); i.r. (CHCl$_3$) ν 2080, 2015, 2000s (Fe–CO), 1680s (CO), 1620s (CO), and 1250s (Me$_3$Si) cm^{-1}; *m/e* 736(2, *M*$^+$), 708 (3, *M*$^+$ – CO), 680(22), 652(1000), 580(14), and 73 (52, Me$_3$Si); ^{1}H-n.m.r. ([^{2}H$_6$]acetone) δ 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) ν 2040s (Fe–CO); 1635s (CO), and 1250s (Me$_3$Si) cm^{-1}; *m/e* 680 (14, *M*$^+$), 652 (100, *M*$^+$ – CO), and 73 (18, Me$_3$Si); ^{1}H-n.m.r. ([^{2}H$_6$]acetone) δ 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$_3$) ν 2960s, 2930m, 2900m, 2160s (C≡C), 1690s (CO), and 1250s (Me$_3$Si) cm^{-1}; *m/e* 568 (4, *M*$^+$), 553 (9, *M*$^+$ – Me), 495 (9, *M*$^+$ – Me$_3$Si), 480(7), and 73 (100, Me$_3$Si); ^{1}H-n.m.r. ([^{2}H$_6$]acetone) δ 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$_3$) ν 2960s, 2930s, 2900s, 2160s (C≡C), 1490m, 1440m, and 1250s (Me$_3$Si) cm^{-1}; *m/e* 572 (6, *M*$^+$), 557 (1, *M*$^+$ – Me), 499 (16, *M*$^+$ – Me$_3$Si), 484(22), 469(11), 411(38), 381(10), and 73 (100, Me$_3$Si); ^{1}H-n.m.r. ([^{2}H$_6$]acetone) δ 7.29—7.15 (8H, m), 0.10 (18H, s), and 0.08 (18H, s).

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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}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 $Fe(CO)_3$ fragment in **(4)** and **(5)** and by Fe(CO)–cyclopentadienone complexation in **(6)**; a new example of the equivalence of $Fe(CO)_3$, Fe(CO)(cyclobutadiene),[6] and Fe(CO)(cyclopentadienone) groups. One cyclopentadienone unit in **(5)** remains uncomplexed; another example of the stable monomeric 2,5-bis(trimethylsilyl)cyclopentadienones described earlier.[9]

I thank the Department of Organic Chemistry of the University of Zürich-Irchel, the Schweizerische Nationalfonds zur Förderung der wissenschaftlichen Forschung, and Prof. Dr. A. S. Dreiding for financial and especially the latter for his generous personal support. Furthermore I am grateful for a fellowship of the Deutsche Forschungsgemeinschaft (1981—1983) and for high resolution mass spectra taken by Dr. W. Vetter (F. Hoffmann-La Roche, Basel).

Received, 28th January 1982; Com. 091

References

1 E. Müller, *Synthesis*, 1974, 761.
2 E. Müller, M. Sauerbier, and J. Heiss, *Tetrahedron Lett.*, 1966, 2473.
3 E. Müller, K. Munk, P. Ziemek, and M. Sauerbier, *Liebigs Ann. Chem.*, 1968, **713**, 40.
4 E. Müller, K. Munk, H.-G. Fritz, and M. Sauerbier, *Liebigs Ann. Chem.*, 1969, **723**, 76.
5 H. W. Whitlock, Jr. and P. E. Sandvick, *J. Am. Chem. Soc.*, 1966, **88**, 4525.
6 E. F. Epstein and L. F. Dahl, *J. Am. Chem. Soc.*, 1970, **92**, 493.
7 E. Müller, M. Sauerbier, D. Streichfuss, R. Thomas, W. Winter, G. Zountsas, and J. Heiss, *Liebigs Ann. Chem.*, 1971, **750**, 63.
8 W. Hübel and E. H. Braye, *J. Inorg. Nucl. Chem.*, 1959, **10**, 250.
9 E. R. F. Gesing, J. P. Tane, and K. P. C. Vollhardt, *Angew. Chem.*, 1980, **92**, 1057, and *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 1023; G. Maier, H.-W. Lage, and H. P. Reisenauer, *Angew. Chem.*, 1981, **93**, 1010.

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