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Preliminary communication

SYNTHESIS AND STRUCTURE OF THREE PRODUCTS OF THE REACTION OF NORBORNADIENE WITH ELEMENTAL SULFUR AND DODECACARBONYLTRIIRON

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Summary

From the interaction products of norbornadiene with S_8 and $Fe_3(CO)_{12}$ three complexes of the composition $Fe_2(CO)_6(S_2C_7H_8)$ were isolated. An X-ray study of these compounds was carried out for establishing the bonding and structure of the norbornadiene group.

In order to continue the study of the interaction of unsaturated hydrocarbons with elemental sulfur in the presence of $Fe_3(CO)_{12}$ [1] the results of the reaction of norbornadiene with dodecacarbonyltriiron and sulfur was examined.

Reaction of norbornadiene (0.3935 mol) with $Fe_3(CO)_{12}$ (0.0635 mol) and S_8 (0.24 g-atom) in benzene (400 ml) at 80°C under Ar gave three complexes (I—III), which were separated by chromatography on a silicagel column (hexane as eluent), and also $Fe_2(CO)_6S_2$ and $Fe_3(CO)_9S_2$. Yields of I—III were determined relative to Fe, R_f values were defined on Silufol plates (Kavalier, Czechoslovakia) for n-heptane. Complex I (2.4%, m.p. 100—101°C, $C_{13}H_8Fe_2O_6S_2$, $R_f = 0.25$), complex II (1.6%, m.p. 183—184°C (dec.), $C_{13}H_8Fe_2O_6S_2$, $R_f = 0.18$), com-

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*Deceased (November 1984).
**Deceased (June 1983).

plex III (2.4%, m.p. 156—158°C (dec.), $C_{13}H_8Fe_2O_6S_2$, $R_f = 0.21$). To establish the bonding and structure of the norbornadiene group in I—III we carried out an X-ray study of compounds I—III.

Crystals of I, II and III are orthorhombic and were grown from hexane. They belong to space group *Pnma* with $Z = 4$ (the molecules have C_s symmetry), *a* 9.308(3), 9.158(3), 9.088(2); *b* 10.544(3), 10.165(4), 10.381(6); *c* 16.890(6), 17.057(5), 17.035(9) Å, *V* 1657(1), 1588(1), 1607(1) Å^3. The structures were resolved by the heavy atom method and refined by least-squares in anisotropic (Fe, S)—isotropic block-diagonal approximation to R_{I} 10.7% for 1160 reflections, R_{II}* 4.8% for 1540 reflections and R_{III} 13.4% for 1300 reflections. The experimental results were obtained on a Syntex-P1 diffractometer (λ(Mo-K_α), graphite monochromator, $\theta/2\theta$-scanning, 2θ max. 50, 60 and 55° for I, II and III, respectively).

Present studies prove, that I, II and III are isomers with binuclear $Fe_2(CO)_6S_2$ fragments bonded in different ways through S-bridges to the carbon atoms of the norbornadiene group. All three molecular structures have C_s crystallographic symmetry with plane *m* crossing Fe(CO) atoms of $Fe(CO)_3$ fragments and the middles of the S···S distances, but division of the C_7H_8 groups in I—III varies. In structure I S-bridges of the $Fe_2(CO)_6S_2$ binuclear fragment are attached to the C(2)—C(3) double bond of norbornadiene bicyclo[2.2.1]hept-5-en-2,3-ylene (BG), i.e. as a result of the reaction one of two olefin bonds of the norbornadiene molecule reacted. Plane *m* in I (Fig. 1) crosses the bridging atom C(7) and the middle of the C(2)—C(3) and C(5)—C(6) bonds of the BG-fragment; the orientation of the C—S bonds in I is axial. A similar addition to one of the double bonds of the norbornadiene molecule has been structurally established in the products of norbornadiene interaction with cyclotrithiatriazene [2] and with tetrasulphur dinitride [3]. More complicated transformation of norbornadiene occurred in the formation of II. Here two double bonds of the norbornadiene molecule reacted and formed two C—S bonds and one C—C internal bond. The tricyclic ligand formed in this way, is tricyclo[2.2.1.0^{3,5}]hept-2,6-ylene (TG) and plane *m* in II (Fig. 1) crosses the bridging atom and the C(1) and C(7) atoms of the TG-group. TG in II retains its C_{3v} symmetry (axis 3 crosses C(1) and the centre of C(3)C(4)C(5) triangular side). In contrast to I and II the structure of III appeared to be disordered with three stoichiometrically substituted C_7H_8 isomers: A, with the C(5★) atom, B, with the C(5) atom and D, with those of C(5′), C(5) and C(5′) atoms bonding along the crystallographic plane *m*: B and D are conformational isomers. The approximate distribution of positions of these three atoms is equal (ca. 1/3). Isomer A in structure III is the TG radical which has symmetry and bonding to S atoms analogous with that found in II, and in accordance with the numbering in Fig. 1 it is tricyclo[2.2.1.0^{3,4}]hept-2,7-ylene. The conformers B and D are BG radicals, similar to those found in I, but with the S atoms bonded to one of the carbon atoms of the former double bond of the norbornadiene molecule and to the bridging atom C(7). And as mirror plane *m*, bonding B and D conformers between themselves (plane *m* intersecting the middle of the C(3)—C(4) bond and C(1) and C(6) atoms, Fig. 1), in the B conformer the C(7) atom is bridging to the six-membered C(1)—C(6) ring, and in the

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*In structure II all atoms were refined in anisotropic approximation.

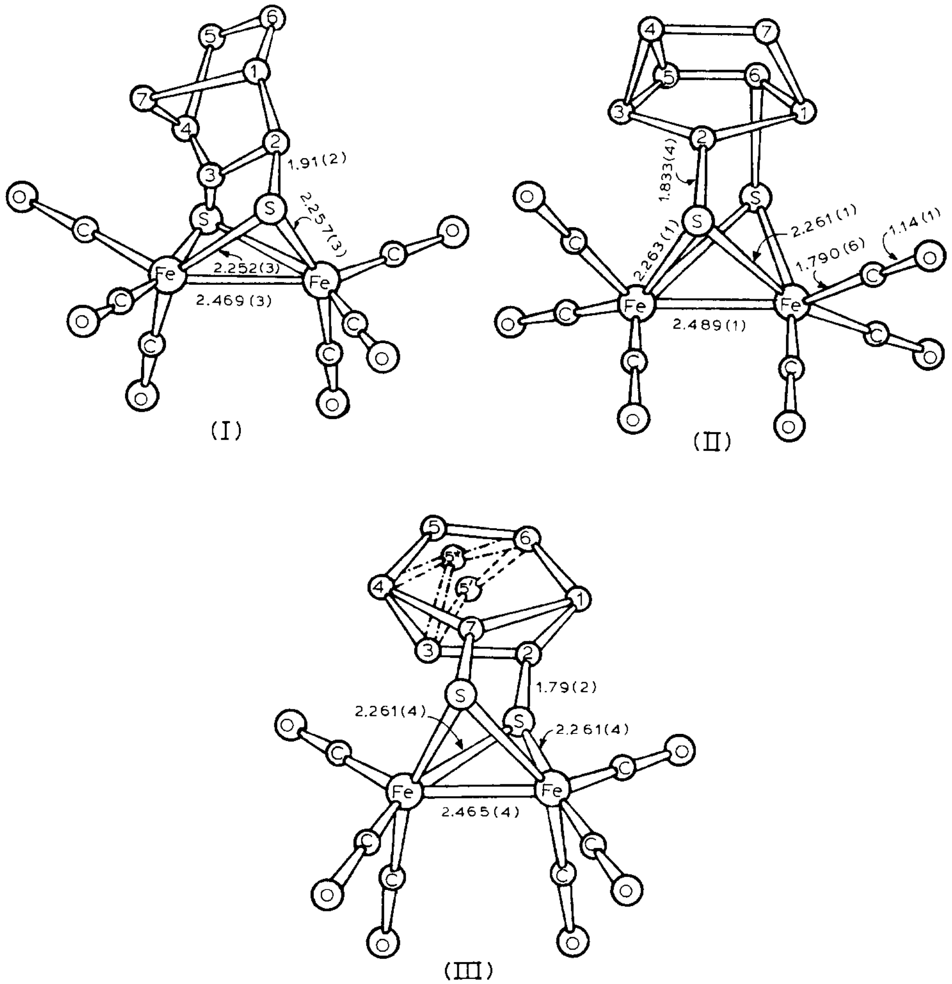

Fig. 1

D conformer C(2) is bridging to C(1)C(6)C(5′)C(3)C(4)C(7). Geometrical parameters of the BG fragment in I are usual and similar to others found earlier [2,3]; and the disorder of the C_7H_8 fragment in III leads to essential differences in bond lengths and valence angles from expected standard values.

$Fe_2(CO)_6S_2$ fragments in structures I, II and III have practically the same configuration with the geometric parameters similar to those found in other $Fe_2(CO)_6(S_2R_2)$ derivatives [4]. Bond lengths of the ordinary Fe—Fe bonds between the $Fe(CO)_3$ fragments are 2.469(3), 2.489(1) and 2.465(4) Å in I, II and III, respectively. In addition average distances from Fe atoms to S-bridges are also similar: 2.255(3), 2.262(1) and 2.261(4) Å,

An interesting feature of structures I—III is their pseudo-isomorphism: they are characterized by similar values of the crystallographic parameters and coordinates of all the atoms except those of the C_7H_8 group.

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