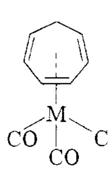
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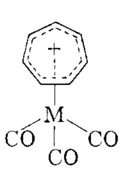
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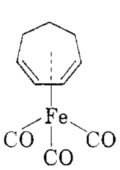
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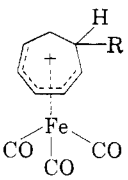
IV

(I, M = Fe) or by hydride ion abstraction from the cycloheptadiene complex (III).[8a]

Heating of equimolar amounts of cycloheptatriene and iron pentacarbonyl under nitrogen at 135° yielded product mixtures in which the ratio, cycloheptatriene complex (I, M = Fe) :cycloheptadiene complex (III), determined mass spectrometrically,[9] decreased with time from 19:1 in 1 day to 2:1 in 5 days. Pure cycloheptatriene complex was obtained by repeated fractional recrystallization of the 1–2 day product mixture from hexane at −78° as an orange liquid, sensitive to light and air (b.p. 60° (0.5 mm), f.p. *ca.* −2°; infrared (neat, CO region), 4.89μ s, 5.08μ s; n.m.r. (CS_2, approx. band centers and relative intensities), 4.2 and 4.8τ (2), 4.7τ (2), 6.8τ (2), 7.6τ (2); calcd. for $(C_7H_8)Fe(CO)_3$: C, 51.77; H, 3.48; O, 20.69; Fe, 24.07; found: C, 52.00; H, 3.52; O, 20.76; Fe, 24.01). The cycloheptadiene complex (III), shown to be present in the product mixture by chemical and physical means, was obtained pure most readily by direct preparation from cycloheptadiene and iron pentacarbonyl in methylcyclohexane under nitrogen at 160° for 36 hr. as a yellow less air-sensitive liquid (b.p. 60° (0.5 mm.), f.p. *ca.* +5°; infrared (neat), 4.90μ s, 5.09μ s; n.m.r. (CCl_4), 4.8τ (2), 7.0τ (2), 8.1τ (4), 8.6τ (2); calcd. for $(C_7H_{10})Fe(CO)_3$: C, 51.32; H, 4.31; O, 20.51; Fe, 23.86; found: C, 51.53; H, 4.48; O, 20.68; Fe, 23.80).

Triphenylcarbonium fluoroborate reacts with the cycloheptatriene complex (I, M = Fe) in dichloromethane to give a 96% yield of the adduct fluoroborate (IV, R = $(C_6H_5)_3C$—) as pale yellow crystals (m.p. gradual darkening above 100°; infrared (KBr), 4.7μ s, 4.87μ s, 5.08μ m; calcd. for $[(C_6H_5)_3C{-}C_7H_8{}^+]Fe(CO)_3,BF_4{}^-$: C, 61.95; H, 4.12; F, 13.11; B, 1.92; found: C, 61.65; H, 4.45; F, 12.78; B, 1.75) and *no* triphenylmethane. Hydride ion abstraction from the cycloheptadiene complex (III) (or from mixtures with the cycloheptatriene complex) by triphenylcarbonium fluoroborate in dichloromethane produced 93% triphenylmethane and 92% of the cycloheptadienium ion complex fluoroborate (IV, R = H)[8] as stable bright yellow crystals (m.p. gradual darkening above 150°; infrared (KBr), 4.76μ s, 4.87μ s, 5.08μ m; n.m.r. (D_2SO_4), 3.1τ (1), 4.2τ (2), 5.2τ (2), 7.5τ (2), 8.2τ (2); calcd. for $(C_7H_9{}^+)Fe(CO)_3,BF_4{}^-$: C, 37.55; H, 2.84; F, 23.76; Fe, 17.46; found: C, 37.83; H, 3.11; F, 23.90; Fe, 17.76), identical with the product obtained immediately in 90% yield by treatment of the cycloheptatriene complex (I, M = Fe) with 48% fluoroboric acid in propionic anhydride. The cycloheptadienium complex salt (IV, R = H) is stable to boiling ethanol but reacts with potassium iodide in acetone at 25° in 3 hr. to give a 45% yield of the substitution product, $(\pi\text{-}C_7H_7)Fe(CO)_2I$, as stable maroon crystals (m.p. 86–89° (dec.); infrared (KBr), 4.96μ s, 5.08μ s, 5.16μ m; n.m.r. ($Cl_3CCOCCl_3$), 3.1τ (2), 6.1τ (2), 7.7τ (2), 8.5τ (2); calcd.: C, 32.56; H, 2.73; Fe, 16.83; found: C, 32.67; H, 2.85; Fe, 16.93).

Structures assigned to the products are supported by the carbonyl absorptions that shift as expected[2b] to shorter wave lengths with cationic ligands and to longer wave lengths on anionic substitution, and by proton resonance spectra containing 4 or 5 groups of absorptions with appropriate chemical shifts[2b,10] in the range 3.0–8.5τ and with correct intensities.

The theoretical conclusion of Brown[11] that excess electrons in iron carbonyl complexes are stabilized only when the organic ligand contains low-lying empty orbitals for back-donation provides explanation of the greater instability and the pronounced electrophile-accepting property of the electron-surfeit cycloheptatriene complex.[12] The more general deduction, by Brown[11] as well as others, that greater stabilization results when excess charge on the metal atom can be dispersed onto electron-accepting ligands, very likely provides rationalization not only of the hydride-donating property of the cycloheptadiene complex and of the enhanced stability of the cycloheptadienium ion complex, but also of the apparent need of an iron *tri*carbonyl moiety in the cycloheptatriene complex as well as all other known, stable, half-sandwich complexes of iron carbonyl with acyclic and monocyclic unsaturated ligands.[13] The mechanism of the formation of the cycloheptadiene complex from cycloheptatriene and iron pentacarbonyl, which may prove to involve an iron carbonyl hydride intermediate as found in other cases,[5,8,14] is under investigation.

[8a] NOTE ADDED IN PROOF.—Hydride ion abstraction from the 1,3-cyclohexadiene complex, $(\pi\text{-}C_6H_8)Fe(CO)_3$, originally prepared by Hallam and Pauson (*J. Chem. Soc.*, 642 (1958)), has furnished the analogous cyclohexadienium ion complex, $[(\pi\text{-}C_6H_7)Fe(CO)_3]^+$, $BF_4{}^-$, which is being investigated as a source of the unknown benzene complex, $(\pi\text{-}C_6H_6)Fe(CO)_3$. Also, E. O. Fischer and R. D. Fischer (*Agnew. Chem.*, **72**, 919 (1960)) have prepared the same cyclohexadienium ion complex.

[9] Intensities of the mass number 204 and 206 peaks, corresponding to the mono-decarbonylated fragments, were used for analysis since the mass 232 parent ion peak of cycloheptatriene-iron-tricarbonyl could not be detected, and the mass 234 parent ion peak of cycloheptadiene-iron-tricarbonyl had only weak intensity.

[10] M. L. H. Green, L. Pratt and G. Wilkinson, *J. Chem. Soc.*, 989 (1960).

[11] D. A. Brown, *J. Inorg. Nuclear Chem.*, **10**, 39, 49 (1959), and **13**, 212 (1960).

[12] The greater stability of the related tropone-iron-tricarbonyl complex (W. Hübel and E. Weiss, *Chemistry and Industry*, 703 (1959)) is attributable to the presence of an additional empty bonding orbital.[11]

[13] *Cf.*, H. Kaesz, R. B. King, T. A. Manuel, L. D. Nichols and F. G. A. Stone, *J. Am. Chem. Soc.*, **82**, 4749 (1960).

[14] H. W. Sternberg and I. Wender, *Chem. Soc.* (*London*) *Spec. Publ.* No. 13, p. 39, 1959.

[15] Standard Oil Company (California) Predoctoral Research Fellow, 1960–1961.

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DOMENICK J. BERTELLI[15]

RECEIVED DECEMBER 3, 1960

REACTION OF DIBORON TETRACHLORIDE WITH AROMATIC SUBSTANCES

Sir:

Diboron tetrachloride has been shown to react with certain unsaturated aliphatic substances,[1,2]

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[1] G. Urry, J. Kerrigan, T. Parsons and H. I. Schlesinger, *J. Am. Chem. Soc.*, **76**, 5299 (1954).

[2] P. Ceron, A. Finch, J. Frey, J. Kerrigan, T. Parsons, G. Urry and H. I. Schlesinger, *ibid.*, **81**, 6328 (1959).

but no description of its behavior with aromatic substances has appeared. We wish to describe the behavior of diboron tetrachloride with benzene and with naphthalene.

At room temperature diboron tetrachloride reacts with an excess of benzene over a period of many days to produce ultimately phenyldichloroborane. Despite the finding that maximum yields of phenyldichloroborane were not achieved except on long standing (84.5% yield, based on benzene consumed, was obtained after 85 days but only 57.8 % after 36 days), it was observed that all of the diboron tetrachloride and all of the benzene consumed disappeared within eight days. Further, about one mole of trichloroborane was released for every mole of diboron tetrachloride used. Though further confirmation is desirable, the above observation and the reaction stoichiometries suggest the reaction path

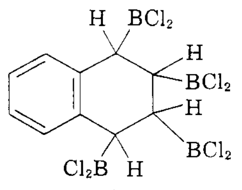
$$2B_2Cl_4 + C_6H_6 \xrightarrow{\text{slow}} C_6H_6.2B_2Cl_4$$

$$C_6H_6.2B_2Cl_4 \xrightarrow{\text{fast}} C_6H_6.2BCl + 2BCl_3$$

$$C_6H_6.2BCl \xrightarrow{\text{slow}} C_6H_5BCl_2 + \text{other products}$$

The phenyldichloroborane was identified by chloride analysis (44.5% found, 44.7% calculated), by the melting point of the phenyldihydroxyborane produced on hydrolysis (215° found, 216° reported[3]), and by comparing the infrared spectrum of this phenyldihydroxyborane with that of a known sample. The remaining reaction products, nonvolatile dark red solids, have not yet been identified. It may be mentioned that benzene was found to be inert to the action of trichloroborane at room temperature under the conditions utilized.

Though with benzene diboron tetrachloride ultimately yields a substitution product, with naphthalene addition takes place. When approximately equimolar quantities of naphthalene and diboron tetrachloride were placed in contact with each other in a sealed tube at room temperature, a bright yellow color was immediately observed despite the fact that both reagents are colorless. Nevertheless, it was found possible to separate the unchanged reagents quantitatively by fractional condensation after a one-hour period,[4] from which behavior we infer the reversible formation of a loose complex. After about two weeks, however, all of the diboron tetrachloride had disappeared. Removal of residual naphthalene by pumping left a pale yellow nonvolatile liquid with a composition corresponding to $C_{10}H_8 \cdot 2B_2Cl_4$. We believe this material has the structure



Support for this structure is based on various types of evidence.

1. All of the chlorine content is lost readily through hydrolysis at room temperature, which suggests that the chlorine is bound to boron rather than to carbon.
2. Treatment with strong aqueous base at 160° released no hydrogen, which suggested the absence of boron-to-boron bonding.
3. The treatment described in (2) produced 1,2,3,4-tetrahydronaphthalene (identified by comparison of its infrared spectrum with that of a standard), which behavior would be predicted for a product of the postulated structure.
4. Although treatment with aqueous base at 100° produced little or no boron-to-carbon bond cleavage, the substance was extremely sensitive to an oxidation. These observations suggest that the boron atoms are bonded to aliphatic rather than aromatic carbon atoms. (Aromatic boron compounds are normally less sensitive to air oxidation and more sensitive to hydrolytic cleavage.[5])
5. The proton magnetic resonance spectra of $C_{10}H_8(BCl_2)_4$ showed a sharp peak characteristic of protons in the benzene ring and a diffuse doublet characteristic of protons in the saturated ring.
6. $C_{10}H_8(BCl_2)_4$ absorbed three, rather than four, moles of trimethylamine. Construction of appropriate molecular models showed that, with four BCl_2 groups in one ring, steric limitations prevent the introduction of more than three trimethylamine molecules.

Though reactions between diboron tetrachloride and naphthalene were allowed to proceed for periods of up to one year, the addition of more than four BCl_2 groups to naphthalene was not observed, nor in shorter experiments was a product containing fewer than four BCl_2 groups per molecule ever observed.

The new substance $C_{10}H_8(BCl_2)_4$ is a pale yellow, viscous liquid which, even at 65° in a high vacuum, could not be distilled. At this temperature it began to discolor slightly; at 145° it was converted rapidly to gaseous trichloroborane and an amorphous yellow-brown solid.

We wish to acknowledge the assistance of Professor Richard Glick in the interpretation of n.m.r. spectra. We are grateful to the Koppers Company, Inc., for their generous support of this work.

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[3] A. Ainley and F. Challenger, *J. Chem. Soc.*, 2171 (1930).

[4] Since liquid diboron tetrachloride would have shown extensive decomposition after one hour at room temperature, naphthalene is clearly behaving as a stabilizer.

[5] M. Lappert, *Chem. Rev.*, **56**, 959 (1956).

PENNSYLVANIA STATE UNIV. WILLIAM BURKE FOX
UNIVERSITY PARK, PA. THOMAS WARTIK

RECEIVED NOVEMBER 18, 1960

STUDIES OF CHLOROBIUM CHLOROPHYLLS. III. CHLOROBIUM CHLOROPHYLL (650)[1]

Sir:

The evidence presented below is consistent with the conclusion that Chlorobium chlorophyll (650) (I) is derived from a homolog of 2-desvinyl-2-α-hydroxyethylpyropheophorbide *a*.[2]

Hydrolysis of (I) in concentrated HCl or dilute, hot methanolic KOH, and subsequent chromatography on sucrose gave two zones of pigment having identical visible absorption spectra. Only results obtained with pigment in the lower, major zone will be discussed. Chlorobium pheophorbide (650) (II)

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[1] N. R. C. Paper No. 6165.

[2] H. Fischer and J. Hasenkamp, *Ann.*, **519**, 42 (1935).