phase sample of tris-(perfluorovinyl)-borine showed no detectable decomposition over a period of a week at room temperature but went entirely to perfluorovinyldifluoroborine and boron trifluoride on being heated to 100° for 5 hr. In the liquid phase perfluorovinyldifluoroborine and boron trifluoride are formed slowly, with about 5% decomposition in four days at room temperature. Perfluorovinyldichloroborine is able to withstand relatively short periods of heating (*e.g.*, 5 hr. at 100°) but on standing for a few days at room temperature it partially decomposes giving boron trifluoride. Formation of the latter substance is of special interest since it shows that B–F bonds can be formed from these compounds by a route not involving simple disproportionation. This latter mode of decomposition is, however, found with bis-(perfluorovinyl)-chloroborine, samples of which were observed to decompose completely into perfluorovinyldichloroborine and tris-(perfluorovinyl)-borine after one day at room temperature. In view of the high stability of vinyldifluoroborine toward disproportionation,[8] it is likely that the tendency of perfluorovinyldifluoroborine to give boron trifluoride does not involve disproportionation, but a fluorine shift type mechanism to electronically unsaturated boron atoms. Such a process, however, probably is inhibited by a contribution of the perfluorovinyl group's π-electrons to the boron atoms's pπ-orbital, with the result that perfluorovinylboron compounds might be thermally more stable than their as yet unknown perfluoroethyl analogs, in which the boron atom's pπ-orbitals would be relatively less satisfied.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HARVARD UNIVERSITY, CAMBRIDGE, MASSACHUSETTS]

Chemistry of the Metal Carbonyls. VI. The Nature of Cycloöctatriene–Iron Carbonyl Complexes[1,2]

BY T. A. MANUEL[3] AND F. G. A. STONE

RECEIVED MAY 13, 1960

Reaction between iron pentacarbonyl and a mixture of cycloöctatrienes at about 140° yields a stable iron complex $C_8H_{10}\cdot Fe(CO)_3$ (I). Treatment of 1,3,5-cycloöctatriene with $Fe_3(CO)_{12}$ in refluxing benzene affords I and an isomeric $C_8H_{10}\cdot Fe(CO)_3$ (II), which may be converted into I by heating with $Fe(CO)_5$. Evidence is presented indicating that I is bicyclo-[4.2.0]octa-2,4-diene-iron tricarbonyl and that II is most probably 1,3,5-cycloöctatriene-iron tricarbonyl.

Recent studies on the chemistry of metal carbonyls have led to the preparation of cyclooctatetraene–iron compounds[4] and of complexes of the diolefin 1,5-cycloöctadiene with iron,[5] chromium,[6] molybdenum[6–8] and tungsten.[6,7] Reactions between certain metal carbonyls and the cycloöctatrienes also have been investigated. However, because of the existence of both 1,3,5- and 1,3,6-cycloöctatriene, as well as the tautomeric equilibrium between 1,3,5-cycloöctatriene and bicyclo[4.2.0]octa-2,4-diene,[9] the cycloöctatriene system might be expected to form more than one type of metal complex. Indeed, Fischer, Palm and Fritz[10] have prepared both 1,3,5- and 1,3,6-cycloöctatriene complexes of the Group VI transition metals. In this work a complex of composition $C_8H_{10}\cdot Fe(CO)_3$ also was reported and formulated as 1,3,6-cycloöctatriene–iron tricarbonyl solely on the basis of a comparison of its infrared spectrum with the spectra of the cycloöctatriene–Group VI metal carbonyl complexes. In this Laboratory a complex $C_8H_{10}\cdot Fe(CO)_3$ (I) was isolated from the reaction between iron pentacarbonyl and a mixture of the cycloöctatrienes at 140°.[4b] On the basis of thermal degradation of the compound, yield data and the failure of the compound to absorb hydrogen over platinum catalyst, it was suggested that I was bicyclo[4.2.0]-octa-2,4-diene–iron tricarbonyl.

The exact correspondence of the infrared spectral bands reported by Fischer, *et al.*,[10] for their $C_8H_{10}\cdot Fe(CO)_3$ complex with those shown by our iron compound (I) indicates the identity of these two compounds. In an attempt to obtain further evidence for our formulation of the compound in question as bicyclo[4.2.0]octa-2,4-diene-iron tricarbonyl, the cycloöctatriene–iron carbonyl system was again investigated.

Experimental[11]

Infrared spectra were taken as liquid films of 0.015 mm. thickness, on a Perkin–Elmer Model 21 spectrophotometer equipped with sodium chloride optics. Ultraviolet spectra were recorded in spectroscopically pure cyclohexane on a Cary Model 11M recording spectrophotometer. Nuclear magnetic resonance spectra were recorded at 40 megacycles on a Varian Model 4300B high resolution spectrometer,

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[2] We are indebted to the Clark Fund of Harvard University for financial support of this work.

[3] National Science Foundation Predoctoral Research Fellow, 1958–1960.

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[11] Microanalyses were performed by Dr. Carol K. Fitz, Needham Heights, Mass.

using solutions in carbon disulfide, with hexamethyldisiloxane as an internal reference.

1. **Reaction between Cycloöctatrienes and Iron Carbonyls.**—A mixture of cycloöctatrienes was prepared as described elsewhere.[9] A sample of the cycloöctatrienes was then treated with iron pentacarbonyl under the same conditions as those previously described[4b] in order to obtain $C_8H_{10}\cdot Fe(CO)_3$ (I). The infrared spectrum of this complex was identical with that of the compound of the same composition obtained previously in these Laboratories.[4b] In several quantitative hydrogenation studies I did not absorb any hydrogen.

2. **Reaction between 1,3,5-Cycloöctatriene and Triiron Dodecacarbonyl.**—A mixture of cycloöctatrienes was treated with potassium tertiary butoxide and in this manner converted to 1,3,5-cycloöctatriene (purity 94% determined from ultraviolet spectrum[9]: ϵ, 3390 at 265 mμ).

A mixture of 1,3,5-cycloöctatriene (1.1 g., 10 mmoles) and $Fe_3(CO)_{12}$ (4.0 g., 8 mmoles) was refluxed under nitrogen in 40 ml. of benzene for 17 hr. Filtration afforded an orange solution which was evaporated to an orange oil under reduced pressure. The oil was chromatographed on alumina. Pentane eluted two yellow bands to give two distinct solutions. Each of these was concentrated, and the residue sublimed (50° (0.1 mm.)). The sublimate from the first eluate consisted of 600 mg. (24% yield) of orange oil I (infrared spectrum identical with that of $C_8H_{10}\cdot Fe(CO)_3$ obtained from $Fe(CO)_5$[4b] (see above), or $Fe_2(CO)_9$,[10] and the mixture of cycloöctatrienes).

Anal. Calcd. for $C_{11}H_{10}O_3Fe$: C, 53.7; H, 4.1. Found: C, 53.8; H, 4.1.

The sublimate (130 mg., 5% yield) obtained from the second eluate was a yellow solid (II), m.p. 24°, also having the composition $C_8H_{10}\cdot Fe(CO)_3$.

Anal. Calcd. for $C_{11}H_{10}O_3Fe$: C, 53.7; H, 4.1. Found: C, 53.4; H, 4.0.

The infrared spectrum of II was found to be clearly different from that of I.[12] Compound I displays absorptions identical (within the limits of accuracy of the instrument) with those reported by Fischer, *et al.*,[10] at 718 (w), 842 (s), 925 (s), 997 (m), 1047 (w), 1131 (s), 1185 (m), 1224 (s), 1280 (m), 1335 (s), 1383 (w), 1443 (s), 2958 (m) and 3004 (w) cm.$^{-1}$. Compound II displays absorptions at 701 (s), 719 (vs), 771 (m), 805 (m), 862 (m), 912 (m), 957 (w), 999 (s), 1043 (m), 1168 (w), 1193 (vw), 1212 (vw), 1314 (w), 1335 (m), 1370 (w), 1403 (w,sh), 1412 (w), 1445 (s), 1460 (w,sh), 1645 (w), 2941 (s), 3049 (m,sh).

Treatment of the chromatography column with a 3:2 pentane–dichloromethane mixture gave an orange solution. Evaporation, followed by sublimation, afforded 60 mg. (2% yield) of the previously reported orange solid assigned by Fischer, *et al.*,[10] the composition $C_{15}H_{12}O_6Fe_2$ (m.p. 73–75°, lit.[10] 72–74°).

3. **Reaction between $C_8H_{10}\cdot Fe(CO)_3$ (II) and Iron Pentacarbonyl.**—A mixture of II (150 mg., 0.6 mmole) and $Fe(CO)_5$ (3 ml., 22 mmoles) in 20 ml. of ethylcyclohexane was refluxed under nitrogen for 17 hr. Filtration of the contents of the flask gave a yellow-green filtrate which was evaporated *in vacuo*. Chromatography of the remaining oil, and then sublimation, gave 20 mg. of yellow oil with an infrared spectrum identical to that of I.

4. **Reaction between $C_8H_{10}\cdot Fe(CO)_3$ (I) and Maleic Anhydride.**—A mixture of I (900 mg., 3.7 mmoles) and maleic anhydride (0.4 g., 4.1 mmoles) in 30 ml. of xylene was refluxed under nitrogen for 19 hr. Filtration gave a yellow solution which was evaporated *in vacuo* to a yellow oil. The infrared spectrum of the oil still possessed bands due to the $Fe(CO)_3$ group, so an additional 0.4 g. sample of maleic anhydride was added and the mixture refluxed in 35 ml. of Soltrol 130 (b.p. 184°) for 20 hr. Filtration afforded a pale yellow solution which on evaporation *in vacuo* gave a mixture of a white solid and a yellow oil. This residue was washed with pentane, and the cream-colored solid remaining was sublimed (90° (0.1 mm.)). This treatment gave 80 mg. of a white solid which proved to be the previously described[9b] maleic anhydride adduct of bicyclo-[4.2.0]octa-2,4-diene.

Anal. Calcd. for $C_{12}H_{12}O_3$: C, 70.6; H, 5.9. Found: C, 70.7; H, 5.8.

The m.p. of the maleic anhydride adduct was 139–142° (lit.[9] 140–143.5°). Furthermore, the m.p. of a mixture of the solid and an authentic sample of the maleic anhydride adduct of bicyclo[4.2.0]octa-2,4-diene was also 139–142°.

5. **Reaction between $C_8H_{10}\cdot Fe(CO)_3$ (I) and Triphenylphosphine.**—A 1-liter Pyrex bulb was charged with 0.6 g. (2.4 mmoles) of I and 2.0 g. (7.6 mmoles) of triphenylphosphine. The bulb was attached to the vacuum line, evacuated, sealed off and heated at 165° for 48 hr. The reaction vessel then was attached to the vacuum line, opened and a clear colorless liquid collected in a trap at −196°. The infrared spectrum of this liquid was as expected for 1,3,5-cycloöctatriene,[9c,13] containing a little bicycloöctadiene. The ultraviolet spectrum of the liquid showed a maximum at 265 mμ with an extinction coefficient of 3500 (lit.[9] value is ϵ = 3600 for 1,3,5-cycloöctatriene and ϵ = 200 for 1,3,6-cycloöctatriene).

Discussion

Since the conditions used originally by us[4b] and by Fischer, *et al.*,[10] to prepare I were very vigorous, it is not surprising that in the earlier work the existence of C_8H_{10} complexes other than I was obscured. As described in the Experimental section, by treating 1,3,5-cycloöctatriene with triiron dodecacarbonyl in refluxing benzene it is possible to obtain two different iron complexes $C_8H_{10}\cdot Fe(CO)_3$. Not surprisingly the compound obtained in lowest yield, II, is the less stable. It is more easily oxidized in air and on heating with iron pentacarbonyl is converted into I. This behavior indicates that I does not contain the 1,3,6-cycloöctatriene group, since 1,3,6-cycloöctatriene would be thermodynamically the least stable of the three C_8H_{10} isomers. Moreover, the stability of I resembles that of the highly stable butadiene-type iron tricarbonyl complexes,[14] suggesting the presence of the bicyclo[4.2.0]octa-2,4-diene moiety in I.

Significantly, the infrared spectrum[12] of II contains most of the bands on the basis of which I was formulated as 1,3,6-cycloöctatriene–iron tricarbonyl.[10] Of special interest in the spectrum of II is a band at 1645 cm.$^{-1}$ in the region where carbon–carbon double bond absorption is found in the free cycloöctatrienes. Such a band would be expected if 1,3,5- or 1,3,6-cycloöctatriene were bonded to an iron tricarbonyl group, but not if bicycloöctadiene were, since in the bicyclic hydrocarbon only two double bonds are present and both would be involved in bonding to iron. Attempts were made to hydrogenate II, but the compound decomposed in the hydrogenation apparatus. Iron complex I, on the other hand, did not decompose during attempts to hydrogenate it, nor did it absorb hydrogen.

The proton n.m.r. spectra of I and II were exceedingly complex, preventing an exact assignment, but the spectrum of II showed a prominent peak at 68 c.p.s. (low-field side of hexamethyldisiloxane) which could be due to the methylene protons in 1,3,5- or 1,3,6-cycloöctatriene-iron tricarbonyl. There is no comparable resonance in the spectrum of I, as would be expected if I were a complex containing the bicyclo[4.2.0]octa-2,4-diene moiety.

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[12] For reproduction of the infrared spectra of the two $C_8H_{10}Fe(CO)_3$ complexes see T. A. Manuel, Ph.D. Thesis, Harvard University, 1961.

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Reaction between I and maleic anhydride gave the adduct of bicyclo[4.2.0[octa-2,4-diene. Cope, *et al.*,[9] found that a mixture of the cycloöctatrienes reacted with maleic anhydride to give a *single* Diels–Alder adduct and that this adduct is that expected from the bicycloöctadiene. Furthermore, it was found that 1,3,6-cycloöctatriene is not converted into the 1,3,5-cycloöctatriene–bicycloöctadiene equilibrium mixture unless heated with strong base. These facts thus provide additional evidence that I is not 1,3,6-cycloöctatriene-iron tricarbonyl.

Degradation of I with triphenylphosphine to yield a 1,3,5-cycloöctatriene–bicycloöctadiene mixture, in agreement with pyrolysis experiments described earlier,[4b] also strongly suggests that the 1,3,6-cycloöctatriene group is not present in I, since triphenylphosphine would be too weak a base to isomerize 1,3,6-cycloöctatriene.

Preparation of I in 24% yield and II in 5% yield from 94% pure 1,3,5-cycloöctatriene again indicates that 1,3,6-cycloöctatriene is not involved in the complexes. However, yield data cannot provide conclusive evidence for the structure of I or II because certain hydrocarbons might isomerize in the presence of iron carbonyl. However, if isomerization of an unsaturated hydrocarbon in the presence of iron carbonyls were to occur, the isomer finally present in the iron complex probably would be the one most similar to butadiene, in view of the high stability of butadiene-iron tricarbonyl.[14a] Thus we have found that iron pentacarbonyl reacts with 1,4-pentadiene to give *trans*-1,3-pentadiene-iron tricarbonyl.[14b] Hence any isomerization of the three C_8H_{10} hydrocarbons by iron carbonyls, if it were to occur, should favor formation of bicyclo[4.2.0]octa-2.4-diene-iron tricarbonyl.

[CONTRIBUTION FROM U. S. BORAX RESEARCH CORPORATION, ANAHEIM, CALIF.]

Tetra-(amino)-diborons[1]

BY R. J. BROTHERTON, A. L. McCLOSKEY, L. L. PETTERSON AND H. STEINBERG

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Tetra-(dimethylamino)-diboron has been prepared in high yields by the reaction of halo-bis-(dimethylamino)-boranes with highly dispersed molten sodium. This diboron compound is stable at 200° in the presence of dry air. Reactions of tetra-(dimethylamino)-diboron with primary and secondary amines have led to a variety of tetra-(amino)-diborons.

Introduction

Knowledge of the chemistry of boron compounds has accelerated rapidly in recent years, and a variety of new boron compounds have been prepared and studied. However, with the exception of certain boron hydrides, only a few examples of materials containing normal covalent boron–boron bonds have been reported. The over-all objective of the present investigation has been the preparation and characterization of such compounds, and the immediate objective has been the study of diboron compounds.

No system of nomenclature for diboron compounds has been generally accepted, and for this reason Urry, *et al.*,[2] have described diboron compounds by chemical formula only. However, the number and complexity of diboron derivatives which are now becoming available necessitates the use of some type of systematic nomenclature, and diboron compounds (except for the tetrahalo-derivatives) will be referred to as substituted diborons in this and in succeeding papers of this series. A suggested alternate method of nomenclature would refer to diboron compounds as derivatives of diborane-(4). Wartik, *et al.*,[3] originally suggested the name tetrachlorodiborine for B_2Cl_4 but subsequently used diboron tetrachloride, a type of nomenclature which has since become generally accepted for this compound and for other halide derivatives.

Diboron tetrachloride and its derivatives are the only reported examples of simple compounds containing boron–boron bonds. Diboron tetrachloride has been prepared by the electric discharge[2–5] and microwave[6] reductions of boron trichloride, and a number of its chemical reactions have been studied.[2,3,7–12] Several unsuccessful attempts to isolate compounds containing boron–boron bonds from reactions of haloboranes and active metals have been reported. Wiberg and Ruschmann[13] has observed that a reaction occurred between sodium and chlorodimethylborane, but boron–boron bonded materials could not be isolated. No reactions were reported in the attempted reductions of bromodiphenylborane[14] or trichloroborazole[15] with sodium, but bulk sodium was apparently used in these experiments. It has been observed in this Laboratory in many cases that bulk sodium is not sufficiently active to react with

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[1] The research reported in this document was supported by Wright Air Development Division of the U. S. Air Force under Contract AF 33(616)-5931. It was presented in part at the 137th Meeting of the American Chemical Society, Cleveland, Ohio, April, 1960.

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