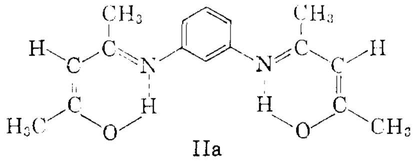
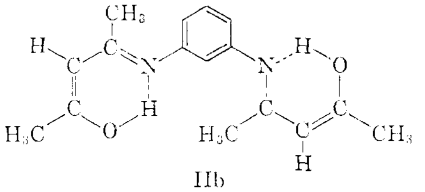
diamine derivatives, and the benzene rings therefore have very little influence, both sterically and electronically, on the molecular moment. The differences between the behavior of the ethylene and trimethylene compounds, with respect to the replacement of methyl by phenyl, is outside experimental error, and is in the direction that would be observed if the increased van der Waals forces between the phenyl groups favored rotational forms having the *cis* configuration.

The structure of bis-acetylacetone-*m*-phenylenediimine differs considerably from those of the other ligands discussed here. As can be seen from structures IIa,b,c rotation is restricted to the two carbon–nitrogen single bonds. The bulky and relatively rigid *m*-phenylene bridge should likewise limit the number of configurations of the end groups favoring *trans* forms and a relatively low dipole moment. However, the relatively high moment observed seems to indicate a constitutional factor which favors a higher moment. This factor may well be the tendency of the aromatic ring to conjugate with the hydrogen bonded chelate rings to stabilize three forms, *cis-cis*, *cis-trans* and *trans-trans*, as is indicated by formulas IIa, IIb and IIc.

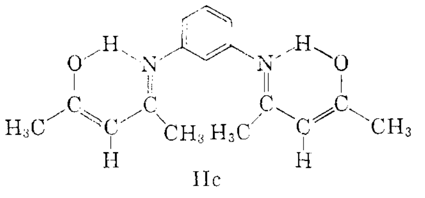
The contributions of two of these, IIa and IIc, which have high moments, could easily account for the high observed moment.



IIa



IIb



IIc

The dipole moments of bis-trifluoroacetylacetonepropylenediimine (5.70 *D*), bis-*p*-bromobenzoylacetonepropylenediimine (3.99 *D*) and bis-*m*-nitrobenzoylacetonetrimethylenediimine (6.96 *D*) are several Debye units higher than the corresponding unsubstituted ligands. This effect is probably the result of the fact that the polar group moments lie in an average direction such that they add to the moments due to the hydrogen-bonded chelate rings. As expected, this factor outweighs the tendency for the average orientation of the end dipoles in the more polar ligands to be somewhat closer to the *trans* form because of the mutual repulsive forces between them.

WORCESTER, MASS.

[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY AT HARVARD UNIVERSITY]

Cycloöctatetraene Iron Tricarbonyl and Related Compounds[1,2]

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

RECEIVED JUNE 29, 1959

From the reaction between iron pentacarbonyl and cycloöctatetraene the three solid compounds $C_8H_8{\cdot}Fe(CO)_3$ (I), C_8H_8-$[Fe(CO)_3]_2$ (II) and $C_8H_8{\cdot}Fe_2(CO)_7$ (III) have been isolated and characterized. Compound I is appreciably volatile and essentially air stable. Its nuclear magnetic resonance spectrum shows a single proton resonance, and it cannot be hydrogenated under conditions under which other metal–cycloöctatetraene complexes (*e.g.*, $C_8H_8{\cdot}PtI_2$) readily absorb hydrogen. These and other properties suggest that all four double bonds of the C_8H_8 ring in I are involved in the bonding to iron. Compound I may also be prepared by heating cycloheptatriene–iron dicarbonyl with cycloöctatetraene. Compound II has no bridging carbonyl groups, and the $Fe(CO)_3$ groups must be on either side of the C_8H_8 ring. Compound III, however, is a derivative of $Fe_2(CO)_9$, possessing bridging carbonyl groups. Certain aspects of the infrared and ultraviolet spectra of I, II and III are discussed. The reaction between iron pentacarbonyl and a mixture of cycloöctatrienes has been investigated. A yellow-orange liquid complex $C_8H_{10}{\cdot}Fe(CO)_3$(IV) was isolated. Its infrared and ultraviolet spectra and its probable constitution are discussed. The reaction between I and the compounds $(C_6H_5)_3M$ (M = P, As and Sb) has been studied. The compounds $[(C_6H_5)_3P]_2Fe(CO)_3$, $(C_6H_5)_3As(C_8H_8)Fe(CO)_2$ and $(C_6H_5)_3Sb(C_8H_8)Fe(CO)_2$ have been isolated. Triphenylphosphine and IV, and triphenylphosphine and $C_4H_6{\cdot}Fe(CO)_3$ afforded $[(C_6H_5)_3P]_3Fe(CO)_2$. The latter material was also obtained, together with $[(C_6H_5)_3P]_2Fe(CO)_3$, when cycloheptatriene–iron dicarbonyl was heated with triphenylphosphine.

The chemistry of the transition elements has been greatly expanded during the last decade by the preparation of derivatives of the metal carbonyls, in which carbon monoxide groups are replaced to some extent by other ligands. For the synthesis of these substituted metal carbonyls two main preparative routes have been used: treatment of a metal carbonyl with the appropriate ligand and treatment of a compound of the metal with carbon monoxide. At this time perhaps the most remarkable of all the ligands occurring bonded to a metal simultaneously with CO are the unsaturated hydrocarbons which do so by means of their π-electrons. One extreme of such behavior is found in the sandwich bonds[4] of the cyclopenta-

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(1) Presented before the 136th Meeting of the American Chemical Society in Atlantic City, N. J., September 1959.

(2) For a preliminary communication see: T. A. Manuel and F. G. A. Stone, *Proc. Chem. Soc.*, 90 (1959).

(3) National Science Foundation predoctoral fellow 1958–1959.

(4) H. H. Jaffe, *J. Chem. Phys.*, **21**, 157 (1953); W. Moffitt, THIS JOURNAL, **76**, 3386 (1954); J. D. Dunitz and L. E. Orgel, *J. Chem.*

dienyl metal derivatives,[5] which were the first such compounds to be recognized. Subsequently compounds containing metal carbonyl groups together with benzene and other aromatic moieties were prepared.[5,6] More recent work has shown that metal carbonyl complexes may be formed in which the metal is bonded to many types of π-electron systems, including those of heterocyclic compounds,[7-9] cycloheptatrienes,[7,10] azulene,[7,11] tropylium ion[12] and even the formally unconjugated bicycloheptadiene.[7,13] Furthermore, it has been shown that under certain conditions acetylenes and metal carbonyls afford π-electron systems, the latter being created during the course of reaction.[14] These cyclization reactions in the presence of metal carbonyls would appear to be rather closely related to the synthesis of ring compounds from acetylenes and nickel salts[15] or from acetylenes and the substances derived from aryl Grignards and certain transition metal halides.[16] In these reactions the metals probably serve as coördination centers for the acetylene molecules, enabling them to condense to ring systems. One of the most interesting substances to be prepared in this manner was cycloöctatetraene.[15] It is well known that this substance has eight π-electrons per molecule, but in striking contrast to benzene the π-electrons form double bonds which are typically olefinic, the tub (D_{2d})[17] structure of the molecule preventing appreciable interaction of the formally conjugated double bonds. Apparently the increase in resonance energy derivable from a planar cycloöctatetraene is insufficient to overcome the additional strain energy which would be generated by the creation of a planar eight-membered ring. In spite of the absence of appreciable electron delocalization in cycloöctatetraene, it seemed worthwhile on several counts to investigate the action of a metal carbonyl on this hydrocarbon. Thus, since the metal carbonyl complexes mentioned above involve five, six and seven-membered rings, it was of interest to extend this work to a cyclic system of eight carbon atoms. Since iron pentacarbonyl forms the very stable derivative $C_4H_6 \cdot Fe(CO)_3$[18] when treated with butadiene, having four π-electrons, this carbonyl appeared particularly suitable for treatment with cycloöctatetraene, having eight π-electrons. From the latter situation arose the possibility of forming a binuclear complex in which two iron atoms would be separated by an eight-membered ring.[19] If such a complex were formed, one of two structures seemed most probable. Either the organic moiety would assume a planar configuration with the two iron atoms above and below the ring, or each of the two iron atoms might bond to the double bonds of cycloöctatetraene in such a manner that the organic moiety would retain its tub-shape. In the latter eventuality the iron to carbon bonding would be similar to that suggested for the iron to carbon bonds in the compound bicycloheptadiene–iron tricarbonyl.[7]

We now wish to describe three different cycloöctatetraene–iron complexes which may be isolated, using chromatography and fractional sublimation, from the reaction between iron pentacarbonyl and cycloöctatetraene. The compound formed in highest yield is cycloöctatetraene–iron tricarbonyl, $C_8H_8 \cdot Fe(CO)_3$ (I), obtained as readily sublimable red crystals (m.p. 92–93.5°; decomp. 160°), very soluble in organic solvents. This mono-iron complex, insoluble in water and dilute acid or base, dissolves unchanged in glacial acetic acid and fails to decolorize bromine in dichloromethane, although subsequently reaction takes place with release of carbon monoxide. The compound is relatively stable to oxidation, being 80% recovered after 20 hr. ultraviolet irradiation in a stream of oxygen. However, potassium permanganate, hydrogen peroxide and perbenzoic acid cause decomposition, although some evidence of intermediate products retaining the metal-carbon monoxide linkage may be obtained.

The failure of $C_8H_8 \cdot Fe(CO)_3$ to decolorize bromine suggests that there are no free double bonds in the complex. The free double bond in π-cyclopentadienylcyclopentadienerhenium dicarbonyl, it should be noted, does react with bromine.[20] If the iron atom in I were uniquely bonded to two double bonds of cycloöctatetraene, one would expect the remaining two double bonds to behave in the normal manner. Furthermore, the hydrogen atoms bonded to the four carbon atoms of the "free" double bonds would be in a different environment from those on the double bonds actually involved in complex formation. To clarify this situation the nuclear magnetic resonance spectrum of I was examined in carbon disulfide. A single proton resonance was observed at a higher field strength

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Phys., **23**, 954 (1955); J. W. Linnett, *Trans. Faraday Soc.*, **52**, 904 (1956).

[5] For a review of these compounds see E. O. Fischer and H. P. Fritz, "Advances in Inorganic Chemistry and Radiochemistry," Vol. 1, Editors, H. J. Emeleus and A. G. Sharpe, Academic Press, Inc., New York, N. Y., 1959, p. 55.

[6] (a) E. O. Fischer and K. Öfele, *Ber.*, **90**, 2532 (1957); (b) E. O. Fischer, K. Öfele, H. Essler, W. Frohlich, J. P. Mortensen and W. Semmlinger, *ibid.*, **91**, 2763 (1958); (c) B. Nicholls and M. C. Whiting, *J. Chem. Soc.*, 551 (1959).

[7] R. Burton, M. L. H. Green, E. W. Abel and G. Wilkinson, *Chemistry and Industry*, 1592 (1958).

[8] E. O. Fischer and K. Öfele, *Ber.*, **91**, 2395 (1958).

[9] B. Moore and G. Wilkinson, *Proc. Chem. Soc.*, 61 (1959).

[10] E. W. Abel, M. A. Bennett, R. Burton and G. Wilkinson, *J. Chem. Soc.*, 4559 (1958).

[11] R. Burton and G. Wilkinson, *Chemistry and Industry*, 1205 (1958).

[12] H. J. Dauben and L. R. Honnen, THIS JOURNAL, **80**, 5570 (1958).

[13] R. Pettit, *ibid.*, **81**, 1266 (1959).

[14] R. Markby, H. W. Sternberg and I. Wender, *ibid.*, **80**, 1009 (1958); G. N. Schrauzer, *Chemistry and Industry*, 1403 (1958); W. Hübel, E. H. Braye, A. Clauss, E. Weiss, U. Kruerke, D. A. Brown, G. S. D. King and C. Hoogzand, *J. Inorg. Nucl. Chem.*, **9**, 204 (1959).

[15] W. Reppe, O. Schlichting, K. Klager and T. Toepel, *Ann.*, **560**, 1 (1948).

[16] H. H. Zeiss and W. Herwig, THIS JOURNAL, **80**, 2913 (1958); M. Tsutsui and H. H. Zeiss, Abstracts of papers presented at the 134th Meeting of the American Chemical Society held in Chicago, September 1958, p. 59-P.

[17] O. Bastiansen, L. Hedberg and K. Hedberg, *J. Chem. Phys.*, **27**, 1311 (1957); W. B. Person, G. C. Pimentel and K. S. Pitzer, THIS JOURNAL, **74**, 3437 (1952).

[18] B. F. Hallam and P. L. Pauson, *J. Chem. Soc.*, 642 (1958).

[19] During the course of our work[2] binuclear metal–azulene complexes were reported (ref. 7 and 11), and a theoretical justification for the existence of binuclear metal complexes having two metal atoms symmetrically separated by a C_nH_n conjugated ring system was also published (D. A. Brown, *Chemistry and Industry*, 126 (1959)).

[20] M. L. H. Green and G. Wilkinson, *J. Chem. Soc.*, 4314 (1958).

than the single proton resonance shown by cyclooctatetraene itself. This observation strongly suggests that the bonding in I involves overlap of suitable iron d-orbitals, perhaps hybridized, with a symmetrical π-orbital extending over all eight carbon atoms so that the cycloöctatetraene ring acquires a planar or nearly planar configuration. It is to be noted that the proton resonances of π-cyclopentadienyl compounds are also shifted to higher field strengths than those of the olefinic protons in cyclopentadiene itself.[21] The infrared spectrum, taken in carbon disulfide solution, of cycloöctatetraene–iron tricarbonyl is also of interest. In the carbon–hydrogen stretching region a single sharp strong absorption at 3012 cm.$^{-1}$ is observed. Moreover, bands which occur in cycloöctatetraene at 1635 and 1609 cm.$^{-1}$ and which have been assigned[22] to the C═C stretch do not appear in $C_8H_8 \cdot Fe(CO)_3$. Of special interest in the infrared spectrum of I is a band of medium strength at 1416 cm.$^{-1}$ which does not appear in cyclooctatetraene. A carbon–carbon stretching frequency in the region 1410–1430 cm.$^{-1}$ appears in the infrared spectra of five- and six-membered ring π-complexes of transition metals and is characteristic of such compounds.[5] The ultraviolet spectrum of $C_8H_8 \cdot Fe(CO)_3$ is significantly different from that of cycloöctatetraene. Unlike the spectrum of the free hydrocarbon, the spectrum of I shows an intense maximum at 304 mμ (ϵ 11,500).

In order to determine whether complex formation with an iron tricarbonyl group confers any aromaticity on the cycloöctatetraene ring in I, an attempt was made to acylate the complex. Unfortunately it was impossible to isolate definite products, although bands characteristic of both the $Fe(CO)_3$ group and organic C═O groups[23] were observed in the infrared spectra of the apparently very air-sensitive reaction mixtures. The failure of $C_8H_8 \cdot Fe(CO)_3$ to yield an isolable Friedel–Crafts derivative is similar to the behavior of benzene–chromium tricarbonyl[6c,23a] and is in contrast to the behavior of $C_5H_5Mn(CO)_3$.[24]

The properties of $C_8H_8 \cdot Fe(CO)_3$ thus support the idea that the ring to metal bonding is similar to that existing in the π-cyclopentadienyl- and arene–metal carbonyls but is very probably closer to that found in the latter class of complexes.[5]

From the foregoing remarks it must not be concluded that cycloöctatetraene always bonds to metals in a manner similar to that found in $C_8H_8 \cdot Fe(CO)_3$. Jensen[25] has reported cycloöctatetraene complexes of platinum halides and has suggested that they are similar in nature to the coördination compounds which platinum salts form with a variety of olefins.[26] We have reinvestigated the complex $C_8H_8 \cdot PtI_2$ described by Jensen[25] and have found not unexpectedly that it may be readily hydrogenated. This is quite in contrast to $C_8H_8 \cdot Fe(CO)_3$ which under the same conditions as those used for the hydrogenation of $C_8H_8 \cdot PtI_2$ absorbs no hydrogen.

Besides the compound $C_8H_8 \cdot Fe(CO)_3$ (I), the binuclear complexes $C_8H_8[Fe(CO)_3]_2$ (II) and $C_8H_8 \cdot Fe_2(CO)_7$ (III) are products of the cycloöctatetraene–iron pentacarbonyl reaction.

The compound $C_8H_8[Fe(CO)_3]_2$ is a yellow air-stable solid (decomp. ~190°) only very slightly soluble in organic solvents. In both chloroform and carbon disulfide solutions the infrared spectrum of II shows two intense carbonyl stretching modes (2047 and 1984 cm.$^{-1}$, in carbon disulfide) in the terminal carbonyl region. In chloroform solution the infrared spectrum of I also shows two intense carbonyl stretching frequencies, a sharp band at 2051 cm.$^{-1}$ and a broader band near 1990 cm.$^{-1}$. In carbon disulfide, however, the latter band is resolved into two very strong, sharp bands at 1992 and 1978 cm.$^{-1}$, so that II shows one less carbonyl stretching frequency than I. In view of the properties of I it is possible that the structure of II is one in which two iron tricarbonyl groups are symmetrically separated by a planar or nearly planar cycloöctatetraene ring. Considering the bonding in II, as a first approximation, in terms of a penetration complex, the ring could be regarded as donating four π-electrons to each metal atom, enabling the two iron atoms to acquire the krypton configuration. As mentioned earlier, however, it is also possible that the cycloöctatetraene ring in II retains the tub-like configuration found in the free hydrocarbon. However, the ultraviolet spectrum of II is very different from that of cycloöctatetraene. Two maxima are observed (359 mμ, ϵ 5320; 256 mμ, ϵ 22,700), as well as an end absorption (ϵ_{210} 35,400) higher than that found in the spectrum of I (ϵ_{210} 26,700) or in the spectrum of cycloöctatetraene (ϵ_{220} 2500 approx.).[27a] Furthermore, the infrared spectrum of II shows a strong band at 1414 cm.$^{-1}$, analogous to that of I at 1416 cm.$^{-1}$. A final decision on the structures of both I and II must await, however, the results of an X-ray crystallographic study.[28]

The binuclear complex $C_8H_8Fe_2(CO)_7$ (III), a black solid, is a derivative of $Fe_2(CO)_9$, since in the infrared spectrum of III there appears a strong carbonyl stretching mode (1802 cm.$^{-1}$ in carbon disulfide) in the bridging region. Thus, III bears the same relation to iron enneacarbonyl as I does to iron pentacarbonyl. Besides the bridging carbonyl band, III shows three other carbonyl stretching modes (2022, 1992 and 1959 cm.$^{-1}$ in carbon disulfide), all intense. The ultraviolet

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[21] W. Strohmeier, E. Lombardi and R. M. Lemmon, *Z. Naturforschg.*, **14a**, 106 (1959); W. Strohmeier and R. M. Lemmon, *ibid.*, **14a**, 109 (1959).

[22] E. R. Lippincott, R. C. Lord and R. S. McDonald, THIS JOURNAL, **73**, 3370 (1951).

[23] The C═O absorptions were observed at 1709 cm.$^{-1}$ from $C_8H_8 \cdot Fe(CO)_3$ and CH_3COCl, and at 1721 and 1681 cm.$^{-1}$ from $C_8H_8 \cdot Fe(CO)_3$ and $C_6H_5CH_2COCl$. These stretching frequencies, recorded in chloroform solution are different from those found in the acid chlorides themselves.

[23a] NOTE ADDED IN PROOF. After this paper was accepted for publication, acetylation of benzene-chromium tricarbonyl was reported (R. Riemschneider, O. Becker and K. Franz, *Monatsh.*, **90**, 571 (1959)).

[24] F. A. Cotton and J. R. Leto, *Chemistry and Industry*, 1368 (1958); E. O. Fischer and K. Pleszke, *Ber.*, **91**, 2719 (1958).

[25] K. A. Jensen, *Acta Chem. Scand.*, **7**, 868 (1953).

[26] J. Chatt, L. M. Vallarino and L. M. Venanzi, *J. Chem. Soc.*, 2496 (1957).

[27] (a) A. C. Cope and W. J. Bailey, THIS JOURNAL, **70**, 2305 (1948); (b) A. C. Cope and F. A. Hochstein, *ibid.*, **72**, 2515 (1950); (c) A. C. Cope, A. C. Haven, F. L. Ramp and E. R. Trumbull, *ibid.*, **74**, 4867 (1952).

[28] Professor W. N. Lipscomb is currently engaged in an X-ray diffraction study of our compounds.

spectrum of III is similar to that of II in displaying two maxima (389 mμ, ϵ 4020; 228 mμ, ϵ 32,800) and high end absorption (ϵ_{210} 32,300). Hence all the cycloöctatetraene iron carbonyl complexes described in this paper exhibit strong absorptions in the ultraviolet region, with end absorptions increasing in magnitude along the series $C_8H_8\cdot Fe(CO)_3$, $C_8H_8\cdot Fe_2(CO)_7$, $(CO)_3Fe\cdot C_8H_8\cdot Fe(CO)_3$.

Isolation of the three cycloöctatetraene–iron carbonyl complexes made it appear worthwhile to attempt the isolation of complexes from reactions between iron pentacarbonyl and other eight-membered ring systems possessing π-electrons. Accordingly, the effect of 1,5-cycloöctadiene on iron pentacarbonyl was studied, but in two reactions no iron carbonyl complex of this diene was isolated. Although it may be possible to prepare a 1,5-cycloöctadiene–iron complex, using conditions different from those employed in this work, failure to isolate such a compound accords with the observation that only metals near the end of each transition series form stable olefin complexes[29] and that only dienes conjugated in certain ways can form complexes with iron.[18,29a]

In view of the discovery of the compound cycloheptatriene–iron dicarbonyl,[7] the effect of iron pentacarbonyl on the cycloöctatrienes was investigated. It is well known that there are two isomeric cycloöctatrienes (1,3,5- and 1,3,6-) and that the 1,3,5-isomer exists in equilibrium with bicyclo(4.2.0)octa-2,4-diene.[27c] Since all these compounds possess double bonds adjacent to each other, there arose the possibility of preparing iron carbonyl complexes of more than one of these isomeric hydrocarbons. However, after a mixture of the cycloöctatrienes had been prepared[27b,c] and subsequently heated with iron pentacarbonyl, only one iron carbonyl complex was isolated in amounts sufficient for identification. All the evidence suggests that this compound, a yellow-orange oil of composition $C_8H_{10}\cdot Fe(CO)_3$, is bicyclo(4.2.0)octa-2,4-diene–iron tricarbonyl (IV). Thus in one experiment, before treatment with iron pentacarbonyl the ultraviolet spectrum of the mixture of C_8H_{10} compounds was taken. The extinction coefficient showed that about 70% of the mixture consisted of the 1,3,5-cycloöctatriene–bicyclo(4.2.0)-octa-2,4-diene system. Now IV was isolated in 53% yield and, therefore, the complex could not be 1,3,6-cycloöctatriene–iron tricarbonyl, unless iron pentacarbonyl converted some of the other C_8H_{10} compounds into 1,3,6-cycloöctatriene, a most unlikely possibility. Furthermore, when IV was dissolved in dichloromethane and the solution subjected to vapor phase chromatography at 160° some degradation was induced, but the only organic compounds issuing from the chromatography apparatus were dichloromethane, IV and a hydrocarbon. This established that IV was a single compound. The infrared spectrum of the hydrocarbon from the decomposition of IV corresponded to that reported for 1,3,5-cycloöctatriene.[27b] This does not prove, however, that the organic moiety in IV is 1,3,5-cycloöctatriene, since at 160° bicyclo(4.2.0)octa-2,4-diene would isomerize rapidly. Nevertheless, the chromatographic experiments support the contention made from the yield data that the 1,3,6-cycloöctatriene group is not present in IV. In almost all the metal–carbonyl complexes of π-electron systems reported so far the metal has a pseudo-inert gas electronic configuration. This suggests that in IV with its $Fe(CO)_3$ group the C_8H_{10} moiety is donating four π-electrons to iron. If the hydrocarbon moiety is 1,3,5-cycloöctatriene, therefore, one of the double bonds of this six π-electron system is not involved in the bonding to iron. On the other hand, if the C_8H_{10} group in IV is a bicyclo(4.2.0)octa-2,4-diene unit, with its four π-electrons, there would be no free double bond in the complex. Accordingly an attempt was made to hydrogenate IV. The compound failed to absorb hydrogen. Furthermore, an incidental qualitative observation was made that IV does not decolorize bromine. There is thus strong evidence that our $C_8H_{10}\cdot Fe(CO)_3$ contains the bicyclo(4.2.0)-octa-2,4-diene unit bonded to an iron tricarbonyl group. The bonding of the organic moiety to iron would, therefore, be similar in nature to that existing in butadiene–iron tricarbonyl.[18] It may not be entirely coincidental that IV and $C_4H_6\cdot Fe(CO)_3$ have similar spectra in the carbonyl region of the infrared and yield the same material when heated with triphenylphosphine (see below). It should be mentioned in passing that the proton n.m.r. spectrum of IV shed no light on the constitution of the compound. The spectrum was exceedingly complicated, perhaps not surprisingly in view of the fact that whichever hydrocarbon moiety was bonded to iron in IV the ring would be buckled, having protons in many different environments above and below carbon atoms of the ring.

The infrared spectrum of $C_8H_{10}\cdot Fe(CO)_3$ (IV), taken in dilute carbon disulfide solution, showed only two carbonyl stretching modes at 2045 and 1974 cm.$^{-1}$ but at least three absorptions (3058, 2924 and 2849 cm.$^{-1}$) in the C–H stretching region. The ultraviolet spectrum showed a shoulder at 284 mμ (ϵ 3240) and a maximum at 226 mμ (ϵ 22,600). The end absorption although high (ϵ_{210} 24,500) was lower than that observed in the spectrum of I.

During the course of our work we studied the effect of a number of reagents on cycloöctatetraene–iron tricarbonyl (I). With iron pentacarbonyl, I afforded the binuclear compound $(CO)_3Fe\cdot C_8H_8\cdot Fe(CO)_3$, but in this reaction, as in the direct reaction of iron pentacarbonyl with cycloöctatetraene, II was formed in poor yield. Treatment of I with mesitylene, hexamethylbenzene or thiophene, all having sufficient π-electrons to replace the three carbonyl groups in $C_8H_8\cdot Fe(CO)_3$, led only to decomposition with partial recovery of starting material. No characterizable product was obtained by treatment of I with sodium cyclopentadienide, but treatment of I with di-

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(29) J. Chatt and L. M. Venanzi, *Nature*, **177**, 852 (1956); *J. Chem. Soc.*, 4735 (1957).

(29a) Note added in proof.—We have since been able to extend the range of metals which form diolefin complexes by preparing 1,5-cycloöctadiene complexes of molybdenum and tungsten (T. A. Manuel and F. G. A. Stone, *Chemistry and Industry*, 1349 (1959)). More recently we have been able to form the two complexes 1,5-cyclo-octadiene-iron tricarbonyl and dipentene-iron tricarbonyl, which were discussed at the 137th Meeting of the American Chemical Society.

cyclopentadiene at its cracking point yielded ferrocene. Although the carbonyl groups of I could not be replaced by ligands possessing a sextet of π-electrons under mild conditions and only decomposition of the complex occurred at elevated temperature, it was found that the reaction of cycloöctatetraene with cycloheptatriene–iron dicarbonyl[7] gave appreciable amounts of $C_8H_8 \cdot Fe(CO)_3$. This reaction is quite remarkable in that under relatively mild conditions $Fe(CO)_3$ groups are formed from $Fe(CO)_2$ groups.

Although treatment of I with amines led to decomposition, treatment with triphenylphosphine resulted in displacement of cycloöctatetraene and formation of the complex $[(C_6H_5)_3P]_2Fe(CO)_3$. The infrared spectrum of this phosphine complex, a yellow solid, showed a single sharp strong carbonyl stretching mode at 1887 cm.$^{-1}$ in carbon disulfide, indicating that it was exclusively *trans*-bis-(triphenylphosphine)-iron tricarbonyl. Treatment of I with triphenylarsine and triphenylstibine, on the other hand, resulted in formation of the compounds $(C_6H_5)_3As(C_8H_8)Fe(CO)_2$ and $(C_6H_5)_3Sb(C_8H_8)Fe(CO)_2$, no displacement of the original organic moiety occurring. The infrared spectra of the arsine and stibine complexes each showed three carbonyl stretching bands between 1900 and 2050 cm.$^{-1}$. Chemical analyses as well as the presence of more than one C–H stretching mode in the infrared spectra and of more than one proton resonance in the n.m.r. spectra clearly showed the presence of C_8H_8 groups in these complexes. The proton resonance attributed to the C_8H_8 group underwent a further shift to higher fields, as compared to that in I.

Stereospecific formation of *trans*-$[(C_6H_5)_3P]_2Fe(CO)_3$ from I is very interesting in view of the fact that when other iron carbonyl complexes were treated with triphenylphosphine, an additional phosphine complex was obtained. Thus in our hands cycloheptatriene–iron dicarbonyl[7] and triphenylphosphine afforded a mixture from which the substances $[(C_6H_5)_3P]_2Fe(CO)_3$ and $[(C_6H_5)_3P]_3Fe(CO)_2$ were isolated. However, from the reaction between triphenylphosphine and butadiene–iron tricarbonyl,[18] and between triphenylphosphine and $C_8H_{10} \cdot Fe(CO)_3$ (IV) the only substance isolated by us had the composition $[(C_6H_5)_3P]_3Fe(CO)_2$. The latter was a mixture of isomers since it showed two strong carbonyl stretching modes in its infrared spectrum (at 1982 and 1923 cm.$^{-1}$ in carbon disulfide), the relative intensities of which changed slightly but significantly from experiment to experiment. It was impossible to resolve this mixture into its components by chromatography, this treatment producing only changes in the relative intensities of the carbonyl bands. If $[(C_6H_5)_3P]_3Fe(CO)_2$ has a trigonal bipyramidal structure, which seems likely in view of the evidence for such a structure in iron pentacarbonyl,[30] there is the possibility that the CO groups could occupy the axial positions of the bipyramid or be adjacent to one another. A mixture of these two possibilities might well give rise to two carbonyl stretching modes of varying intensities.

Experimental[31]

1. **Spectroscopic Studies.**—Infrared spectra were recorded using a Perkin-Elmer Model 21 spectrophotometer equipped with sodium chloride optics. Ultraviolet spectra were taken in spectroscopically pure cyclohexane on a Cary Model 11M recording spectrophotometer. Nuclear magnetic resonance spectra were recorded at 40 megacycles by a Varian Model 4300B high resolution spectrometer fitted with a super stabilizer. For n.m.r. work saturated solutions of the compounds to be studied were prepared in carbon disulfide. Hexamethyldisiloxane was used as an internal standard. Line positions were determined by the audiofrequency side-banding technique and are referred in this paper to the position of cyclohexane in infinite dilution in carbon tetrachloride, the shifts in all cases being to the low-field side.

2. **Reaction between Cycloöctatetraene and Iron Pentacarbonyl.**—A mixture of 6.45 g. (62 mmoles) of C_8H_8 and 17.5 g. (89 mmoles) of $Fe(CO)_5$ in 150 ml. of ethylcyclohexane was refluxed under a stream of prepurified nitrogen for 24 hr. Removal of solvent at 0.1 mm. afforded a reddish-brown residue. Sublimation (60–80° (0.1 mm.)) of the residue gave 9.0 g. of red crystalline $C_8H_8 \cdot Fe(CO)_3$ (yield 60%).

Anal. Calcd. for $C_{11}H_8O_3Fe$: C, 54.1; H, 3.3; Fe, 22.9; mol. wt., 244. Found: C, 54.3; H, 3.3; Fe, 22.9; mol. wt. (cryoscopic in benzene), 238.

The yellow-brown residues remaining from the sublimation were chromatographed several times on alumina. Elution with 30–60° petroleum ether gave yellow solutions from which was crystallized 1.92 g. (8% yield) of the yellow solid $C_8H_8[Fe(CO)_3]_2$, decomp. ~190°.

Anal. Calcd. for $C_{14}H_8O_6Fe_2$: C, 43.8; H, 2.1; Fe, 29.2; mol. wt., 384. Found: C, 43.6; H, 2.2; Fe, >24; mol. wt. (cryoscopic in benzene), 413.

Elution of the chromatography column with chloroform gave brownish solutions from which was crystallized an additional 2.26 g. (~9% yield) of a mixture of II and $C_8H_8 \cdot Fe_2(CO)_7$ (III). Fractional sublimation of this mixture led to some decomposition but also gave low yields of III (decomp. ~ 220°).

Anal. Calcd. for $C_{15}H_8O_7Fe$: C, 43.7; H, 2.0; Fe, 27.0. Found: C, 43.8; H, 2.2; Fe, 27.3.

3. **The Nuclear Magnetic Resonance Spectrum of $C_8H_8 \cdot Fe(CO)_3$.**—The n.m.r. spectrum of I, recorded as described above, exhibited a single proton resonance at 152 ± 2 c.p.s.[32] Cycloöctatetraene showed a single proton resonance at 171 ± 2 c.p.s. on the low field side.

4. **Hydrogenation Studies on $C_8H_8 \cdot Fe(CO)_3$ and $C_8H_8PtI_2$.**—Micro-hydrogenation experiments were carried out in an apparatus of the type described by Clauson-Kaas and Limborg.[33]

A 22.9-mg. (9.38×10^{-2} mmole) sample of $C_8H_8 \cdot Fe(CO)_3$ was dissolved in 2 ml. of glacial acetic acid and the solution stirred with 20 mg. of platinum catalyst in an atmosphere of hydrogen for 3 hr. No hydrogen was absorbed.[34]

In a similar experiment, 21.0 mg. (3.79×10^{-2} mmole) of $C_8H_8PtI_2$[25] dissolved partially in 2 ml. of glacial acetic acid and stirred with platinum catalyst under hydrogen *began to absorb hydrogen immediately*. In 3 hr. the uptake of hydrogen was 0.99 cc. (S.T.P.) and in 24 hr. 1.25 cc. (S.T.P.), equivalent to 73.5% of the expected uptake for two "free" double bonds in $C_8H_8 \cdot PtI_2$.

5. **Attempted Preparation of a 1,5-Cycloöctadiene–Iron Carbonyl Complex.**[29a]—A mixture of 26.5 g. (245 mmoles) of 1,5-cycloöctadiene and 21.9 g. (112 mmoles) of $Fe(CO)_5$ was refluxed for 6 hr. under a stream of nitrogen. A metallic mirror developed on the flask, and the solution became dark green. Volatile materials were removed at 0.1 mm., and the residue was boiled in chloroform with charcoal. Filtra-

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(30) H. Stammreich, O. Sala and Y. Tavares, *J. Chem. Phys.*, **30**, 856 (1959).

(31) Microanalyses were performed by Dr. Carol K. Fitz, Needham Heights, Mass., and the Scandinavian Microanalytical Laboratory, Copenhagen, Denmark.

(32) It is hardly necessary to point out that these results confirm the diamagnetism of cycloöctatetraene–iron tricarbonyl.

(33) N. Clauson-Kaas and F. Limborg, *Acta Chem. Scand.*, **1**, 884 (1947). We are indebted to Professor R. B. Woodward for making this equipment available for our use.

(34) Under similar conditions cycloöctatetraene absorbs four equivalents of hydrogen in less than 1 hr. (ref. 15).

tion and evaporation gave only a very small amount of a greenish-black solid, probably $Fe_3(CO)_{12}$.

A repeat reaction between $Fe(CO)_5$ and 1,5-cycloöctadiene, carried out in "Soltrol 130" at its boiling point, 176°, also yielded no cycloöctadiene–iron carbonyl derivative.

6. **The Reaction between Iron Pentacarbonyl and a Mixture of Cycloöctatrienes. Studies on the Nature of the Compound $C_8H_{10}\cdot Fe(CO)_3$ (IV).**—A mixture of isomeric cycloöctatrienes (1.1 g., 10 mmoles) was prepared according to the method of Cope, *et al.*[27b,c] The extinction coefficient measured at 265 mμ was 2660, indicating the presence of 72% of 1,3,5-cycloöctatriene and bicyclo(4.2.0)octa-2,4-diene. The mixture was refluxed under nitrogen for 18 hr. with 40 ml. of ethylcyclohexane and iron pentacarbonyl (2.92 g., 15 mmoles). After the flask had cooled to ambient temperature, solvent was removed at 0.1 mm. The contents of the flask were washed out with chloroform, which was boiled with charcoal and filtered; and the brown filtrate was chromatographed on alumina. Petroleum ether eluted a yellow solution which gave after evaporation of solvent 1.3 g. of a yellow-orange oil (IV) (53% yield based on total C_8H_{10} mixture taken for reaction). Elution of the chromatography column with chloroform and removal of solvent gave a trace of a yellow oil, having the same infrared spectrum as IV in the carbonyl region, but a different spectrum in other regions. In a repeat experiment IV was obtained in 61% yield. For these two representative preparations of $C_8H_{10}\cdot Fe(CO)_3$, *Anal.* Calcd. for $C_{11}H_{10}O_3Fe$: O, 53.7; H, 4.1. Found: C, 53.8, 53.7; H, 4.1, 4.1.

After analysis, in order to determine if IV was a single compound and also to degrade the complex thermally, successive samples were dissolved in chloroform and chromatographed on a diisodecyl phthalate column using a Perkin-Elmer Model 154-C vapor fractometer at 160° with helium flow of 140 cc./min. For each run, after dichloromethane was eluted, only two peaks were recorded. The first of these peaks was due to a cycloöctatriene isomer, established by the fact that the retention time was the same as when the cycloöctatrienes themselves were chromatographed. Material corresponding to this peak was collected in quantity sufficient for recording its infrared spectrum using a micro cell. The spectrum was identical with that reported for 1,3,5-cycloöctatriene.[27b] Material corresponding to the second peak was also collected and its infrared spectrum taken. The spectrum was identical to that of the starting material before chromatography. On dismantling the fractometer it was found that partial pyrolysis had indeed occurred in the pre-heater. In other experiments with the fractometer, varying degrees of pyrolysis were effected, and the triene freed from IV was sometimes isomerized in varying degrees.

Compound IV may be sublimed at 60–70° (0.1 mm.). After it was found that IV did not decolorize bromine in chloroform, a catalytic hydrogenation[33] was attempted using a 19.6-mg. sample. Over a period of 19 hr. no hydrogen was absorbed. The cycloöctatrienes themselves may be rapidly hydrogenated.[27b]

7. **Formation of Cycloöctatetraene–Iron Tricarbonyl from Cycloheptatriene–Iron Dicarbonyl.**—Although the existence of the compound $C_7H_8\cdot Fe(CO)_2$ has been reported in the literature,[4] preparative details have not been described. For this work the compound was obtained as follows. A mixture of 30 ml. of commercial cycloheptatriene (exact purity unknown, ~300 mmoles) and 30 ml. of $Fe(CO)_5$ (43.8 g., 220 mmoles) was refluxed under prepurified nitrogen for 21 hr. The mixture turned brown, and on cooling to room temperature all material volatile at 0.1 mm. was removed. Distillation (0.15 mm. (66–70°)) afforded 32 g. (52% yield, based on 300 mmoles of C_7H_8) of the orange-red liquid $C_7H_8\cdot Fe(CO)_2$.

Anal. Calcd. for $C_9H_8O_2Fe$: C, 52.9; H, 4.0. Found: C, 52.7; H, 3.8.

A mixture of 2.04 g. (10 mmoles) of cycloheptatriene–iron dicarbonyl and 1.42 g. (14 mmoles) of cycloöctatetraene in 40 ml. of ethylcyclohexane was refluxed for 4.5 hr. under a stream of nitrogen. The contents of the flask became black. Solvent was removed at 0.1 mm. The red-black residue was partially dissolved in $CHCl_3$. The resulting solution was boiled with charcoal and filtered. The dark-red filtrate was concentrated to a red oil. Approximately one-third of this oil was sublimed *in vacuo*, yielding 0.5 g. of $C_8H_8\cdot Fe(CO)_3$ (identified by its infrared spectrum). Chromatography of the remainder of the product with an infrared spectral study of the eluates showed that the sole reaction product was cycloöctatetraene–iron tricarbonyl.

8. **Reactions between $C_8H_8\cdot Fe(CO)_3$ and the Triphenyl Derivatives of P, As and Sb.** (a) **Triphenylphosphine.**—A mixture of 1.31 g. (5 mmoles) of triphenylphosphine and 1.22 g. (5 mmoles) of I in 40 ml. of ethylcyclohexane was refluxed under prepurified nitrogen for 9 hrs. The reaction mixture was cooled to −78° and filtered, yielding a brown residue and a red ethylcyclohexane filtrate. The residue was dissolved in CH_2Cl_2 and chromatographed on alumina. Elution with petroleum ether afforded a yellow solution from which was obtained after two crystallizations 0.8 g. (48% yield) of pale yellow crystalline $[(C_6H_5)_3P]_2Fe(CO)_3$.

Anal. Calcd. for $C_{39}H_{30}O_3P_2Fe$: C, 70.6; H, 4.5; P, 9.3; Fe, 8.4. Found: C, 70.4; H, 4.8; P, 9.2; Fe, 9.6.

Bis-triphenylphosphine–iron tricarbonyl is non-volatile and apparently stable in air for a period of weeks. Its solutions, however, undergo partial decomposition in air within hours. When heated it darkens above 225° and melts with gas evolution between 280 and 285°.

Solvent was removed at 0.1 mm. from the red filtrate. Chromatography of the residue on alumina yielded small amounts of I (identified by its infrared spectrum) and an unstable red oil. A carbon disulfide solution of the latter exhibited three carbonyl stretches in the infrared. As described below, the derivatives $(C_6H_5)_3M(C_8H_8)Fe(CO)_2$ (M = As or Sb) show three carbonyl stretching modes in their infrared spectra. It is probable, therefore, that the unstable red oil mentioned here was the compound $(C_6H_5)_3P(C_8H_8)Fe(CO)_2$.

(b) **Triphenylarsine and Triphenylstibine.**—A mixture of 3.06 g. (10 mmoles) of triphenylarsine and 1.22 g. (5 mmoles) of I in 40 ml. of ethylcyclohexane was refluxed under nitrogen for 15 hr. Solvent was removed *in vacuo* leaving a red oil. The latter was dissolved in CH_2Cl_2, filtered and the filtrate chromatographed on alumina. Petroleum ether eluted a red solution. After removal of solvent a red oil remained. The latter was pumped at 80° (0.1 mm.) for several hours. Some of I sublimed away, yielding 2.1 g. (80% yield) of the compound $(C_6H_5)_3As(C_8H_8)Fe(CO)_2$ as a red oil, which with difficulty could be induced to form sticky crystals.

Anal. Calcd. for $C_{28}H_{23}O_2AsFe$: C, 64.4; H, 4.4; Fe, 10.7. Found: C, 63.5; H, 4.8; Fe, 10.8

The compound $(C_6H_5)_3Sb(C_8H_8)Fe(CO)_2$ was prepared in 50% yield from I and $(C_6H_5)_3Sb$ by using similar techniques to that just described for the arsine analog.

Anal. Calcd. for $C_{28}H_{23}O_2SbFe$: C, 59.1; H, 4.1. Found: C, 60.1; H, 4.3.

Solutions of these arsine and stibine compounds are moderately air sensitive, as are to a lesser extent the compounds themselves. In carbon disulfide solution the infrared spectrum of $(C_6H_5)_3As(C_8H_8)Fe(CO)_2$ shows C–H stretching modes at 3058 cm.$^{-1}$ (m) and 3012 cm.$^{-1}$ (m); and carbonyl bands at 2043 cm.$^{-1}$ (m), 1984 cm.$^{-1}$ (s) and 1928 cm.$^{-1}$(s). In the spectrum of $(C_6H_5)_3Sb(C_8H_8)Fe(CO)_2$ comparable bands appear at 3055 cm.$^{-1}$(m), 3030 cm.$^{-1}$(m.sh.) and 2929 cm.$^{-1}$(w); and at 2045 cm.$^{-1}$(m), 1978 cm.$^{-1}$(s) and 1920 cm.$^{-1}$(s).

The nuclear magnetic resonance spectrum of $(C_6H_5)_3As(C_8H_8)Fe(CO)_2$ shows peaks at 237 c.p.s., 231 c.p.s. and 137 c.p.s. Triphenylarsine itself was observed to have a peak at 232 c.p.s. The nuclear magnetic resonance spectrum of $(C_6H_5)_3Sb(C_8H_8)Fe(CO)_2$ showed proton resonances at 234 and 138 c.p.s., while $(C_6H_5)_3Sb$ has a peak at 231 c.p.s. The compound $[(C_6H_5)_3P]_2Fe(CO)_3$ exhibited a single n.m.r. peak at 237 c.p.s. All these resonances are referred to cyclohexane (see Section 1 above).

9. **The Reaction between Triphenylphosphine and Cycloheptatriene–Iron Dicarbonyl.**—A mixture of 2.04 g. (10 mmoles) of $C_7H_8\cdot Fe(CO)_2$ and 2.62 g. (10 mmoles) of triphenylphosphine in 40 ml. of ethylcyclohexane was refluxed for 7 hr. under nitrogen. The reaction mixture was then cooled to −78° and filtered. This afforded a brown residue and an ethylcyclohexane filtrate. The residue was boiled with CH_2Cl_2, filtered and the filtrate chromatographed on alumina. Petroleum ether eluted a yellow solution, from which was crystallized 0.46 g. of $[(C_6H_5)_3P]_2Fe(CO)_3$, infrared spectrum identical with that observed previously for this compound. An additional 0.5 g. was obtained slightly impure (total yield 29% based on $(C_6H_5)_3P$).

Anal. Calcd. for $C_{39}H_{30}O_3P_2Fe$: C, 70.6; H, 4.5; P, 9.3; Fe 8.4. Found: C, 70.6; H, 4.7; P, 9.2; Fe, 9.5.

The ethylcyclohexane solution was evaporated to dryness and the resultant residue dissolved in chloroform and chromatographed on alumina. Petroleum ether eluted a yellow oil having the same carbonyl frequencies in its infrared spectrum as $C_7H_8 \cdot Fe(CO)_2$. Chloroform eluted an unstable orange solution from which was obtained after crystallization and evaporation under nitrogen 0.4 g. (yield 13%) of a yellow-orange solid, $[(C_6H_5)_3P]_3Fe(CO)_2$. The latter exhibited intense carbonyl stretching modes at 1982 and 1923 cm.$^{-1}$ in carbon disulfide solution. As mentioned earlier, the relative intensities of the carbonyl bands depended on the extent of chromatography employed on $[(C_6H_5)_3P]_3Fe(CO)_2$ and on the method used to prepare the material.

Anal. Calcd. for $C_{56}H_{45}O_2P_3Fe$: C, 74.8; H, 5.1; P, 10.4. Found: C, 74.7; H, 5.9; P, 9.4.

10. The Reaction between Triphenylphosphine and Butadiene–Iron Tricarbonyl or the Compound $C_8H_{10} \cdot Fe(CO)_3$. (a) Butadiene–Iron Tricarbonyl.—Triphenylphosphine (1.3 g., 5.0 mmoles) was treated with butadiene–iron tricarbonyl[18] (5.0 mmoles) in the manner described above for similar reactions. A considerable amount of starting material was recovered, but in addition 60 mg. (4% yield based on $(C_5H_5)_3P$) of $[(C_6H_5)_3P]_3Fe(CO)_2$ (infrared spectrum identical with that observed previously for this compound) was obtained.

Anal. Calcd. for $C_{56}H_{45}O_2P_3Fe$: C, 74.8; H, 5.1; P, 10.4. Found: C, 74.3; H, 5.5; P, 9.1.

(b) **$C_8H_{10} \cdot Fe(CO)_3$.**—Treatment of triphenylphosphine (1.2 g., 4.7 mmoles) with $C_8H_{10} \cdot Fe(CO)_3$ (1.2 g., 4.7 mmoles) in the manner described above for similar reactions afforded starting materials and after several recrystallizations 150 mg. (11% yield) of $[(C_6H_5)_3P]_3Fe(CO)_2$ (infrared spectrum identical with that previously obtained for this compound except for relative band intensities).

Anal. Calcd. for $C_{56}H_{45}O_2P_3Fe$: C, 74.8; H, 5.1; P, 10.4 Found: C, 73.8; H, 5.6; P, 9.0.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

Organoboron Compounds. XII. Identification of the Presumed Alkoxydifluoroboranes as Coördination Compounds of Trialkyl Borates and Boron Fluoride[1,2]

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The substances reported in the literature as alkoxydifluoroboranes have properties which are more characteristic of coördination compounds than of substituted boranes. A consideration of vapor densities, cryoscopic molecular weights, distillation behavior, electric moments and reaction with nitrogen bases leads to the identification of the presumed alkoxydifluoroboranes as coördination compounds of trialkyl borates and two moles of boron fluoride. Comparison of these substances with the well established ether–boron fluoride coördination compounds supports their identification as coördination compounds.

A number of compounds formed by the reaction of boron fluoride with alcohols[3] or with alkyl borates[4–7] are identified in the literature as alkoxydifluoroboranes, $ROBF_2$.[8] These fluorine compounds are distillable without disproportionation while the alkoxydichloroboranes, $ROBCl_2$, undergo disproportionation and cleavage reactions when distilled.[9,10]

From a consideration of the relative disproportionation tendencies of other fluoro- and chloroboranes and analogous silicon compounds, it is not to be expected that alkoxydifluoroboranes would be more resistant to disproportionation than alkoxydichloroboranes. Where comparisons have been available it has been noted that disproportionation occurs much more readily with fluorine compounds than with chlorine compounds of boron and silicon. It has been found, for example, that dialkylchloroboranes are much more resistant to disproportionation (to alkyldichloroboranes and trialkylboranes) than are the dialkylfluoroboranes.[11] Also silyl chloride[12] is appreciably more resistant to disproportionation than is silyl fluoride and *sym* - tetraalkyldichlorodisiloxanes are much more resistant to disproportionation than are the corresponding fluorine compounds.[13] The case of the alkoxydihaloboranes would thus appear to represent a reversal of the comparative tendencies toward disproportionation noted in other boron and silicon compounds. Since we are currently engaged in a general study of the disproportionation reactions of organoboron and organosilicon compounds in this Laboratory, the presumed alkoxydifluoroboranes were examined to check their apparent anomalous resistance to disproportionation. The results obtained indicate that the presumed alkoxydifluoroboranes have been incorrectly identified and that the resistance to disproportionation of these substances does not, therefore, represent a reversal of the general trend.

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(1) Previous paper, THIS JOURNAL, **81**, 1768 (1959).

(2) Contribution from the Radiation Project operated by the University of Notre Dame and supported in part under Atomic Energy Commission Contract AT-(11-1)-38.

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