Ph_4AsCuX_3 salts, the pathway is probably not a direct through-space interaction, the X–X distances between adjacent dimers being just too long. Rather, the interactions probably involve either the protons or the π system on the phenyl groups.

Ginsberg and Lines[16] have shown that, if the susceptibility of the cluster is given by

$$\chi_M = \frac{Ng^2\mu_\beta^2}{kT}F(J, T)$$

then interdimer interactions, J', can be accounted for, in a molecular field approximation, by the equation

$$\chi_M = \frac{Ng^2\mu_\beta^2}{k(T-\Theta)}F(J, T)$$

with $\Theta = 2J'z'(F(J, T))/k$, where z' is the number of nearest clusters. Thus Θ is (hopefully) only weakly temperature dependent. In the temperature regime $2J' \ll \Delta E \sim kT$, the susceptibility for a linear chain of dimers (eq 1) reduces to

$$\chi_M = \frac{Ng^2\mu_\beta^2}{k(T-\Theta)} \frac{e^{\Delta E/kT}}{1 + 3e^{\Delta E/kT}}$$

again with $\Delta E = 2J$. In this regime

$$\Theta = \frac{2J'}{k}\left[1 - \frac{1 + e^{\Delta E/kT}}{1 + 3e^{\Delta E/kT}}\right] = \frac{2J'}{k}\left[\frac{2e^{\Delta E/kT}}{1 + 3e^{\Delta E/kT}}\right]$$

Thus, the results for the one-dimensional Ising model are identical with that of the molecular field approximation. For our system, $\Theta \approx {}^4/_3J'$. In $KCuBr_3$, whose structure consists of a linear chain of dimers, $\Theta = 17°$ was deduced from the susceptibility measurements.[13] This corresponds then to $2J' = 18$ cm^{-1}.

It should be emphasized that the interdimer coupling could easily have missed if a plot of χT *vs.* T had not been made. While existence of triplet ground-state systems is relatively rare, if interdimer interactions are suspected, it is recommended that such plots be examined, since the effects discussed here will not be apparent on a $1/\chi$ *vs.* T plot.

Registry No. $(Ph_4As)_2Cu_2Br_6$, 52873-77-5; $(Ph_4As)_2Cu_2Br_2Cl_4$, 53154-28-2.

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Stable Intermediates in the Oxidative Degradation of Dodecahydrododecaborate(2−), $B_{12}H_{12}^{2-}$

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Received June 26, 1974 AIC40417S

The unusual behavior of neutral or alkaline aqueous $KMnO_4$, which, unlike most stronger and weaker oxidizing agents, fails to yield coupled products but instead degrades the polyhedral ions $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ to boric acid, has been reported before.[1] The reaction with $B_{10}H_{10}^{2-}$ is so rapid that it has been used for a calorimetric determination of the reaction heat,[2] but $B_{12}H_{12}^{2-}$ reacts much slower so it appeared a logical reactant in our attempt to isolate the suspected reaction intermediates. Since hydroxylation is known to reduce the oxidative stability of the $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ ions,[3] a search for hydroxy derivatives appeared to be a reasonable first step in any attempt to elucidate the full mechanism of this interesting reaction. The results of this search are reported below.

Results and Discussion

The boric acid content of reaction mixtures with a progressively larger $MnO_4^-:B_{12}H_{12}^{2-}$ ratio was determined. The data shown in Table I reveal that except at very high ratios the yield of boric acid lags far behind the amount expected if no stable intermediates had been formed. Column 2 gives the maximum yield based on the stoichiometry of eq 1. Each

$$3B_{12}H_{12}^{2-} + 50MnO_4^- + 64H_2O = 36B(OH)_4^- + 50MnO_2 + 20OH^- \tag{1}$$

experimental value in column 3 represents the average from three mixtures of same reagent ratio. The mixtures were made up with the two sets of solutions listed in the Experimental Section.

Three complete series of runs were made. In each series the amount of $B_{12}H_{12}^{2-}$ was maintained constant while that of MnO_4^- was raised by dilution with a stock MnO_4^- solution in fixed increments. Each increment was *equivalent* to the amount needed to substitute one hydroxy group in accordance with eq 2, and it may be referred to as "hydroxylation equivalent."

$$3B_{12}H_{12}^{2-} + 2nMnO_4^- + nH_2O = 3B_{12}H_{12-n}(OH)_n^{2-} + 2nMnO_2 + 2nOH^- \tag{2}$$

Thus each series of runs began with a 2:3 and ended with a 50:3 molar reagent ratio. Though the only intermediates that we have been able to identify positively are $B_{12}H_{11}OH^{2-}$ and $B_{12}H_{10}(OH)_2^{2-}$, the progressive changes in the ir spectra and the tlc characteristics of the precipitated cesium salts leave little doubt that a number of more highly substituted ions are formed too.

If the MnO_4^- required for the observed boric acid formation according to eq 1 is subtracted from the total permanganate added and the remainder is assumed to have been used for hydroxylation according to eq 2, the average value of n shown in the fourth column of Table I can be obtained with the aid of a simple formula: $n_{av} = (n_0 - 25X_{BA})/(1 - X_{BA})$, where n_0 is the number of hydroxylation equivalents shown in the first column of Table I and X_{BA} is the fraction of $B_{12}H_{12}^{2-}$ converted to boric acid, computed from data in column 3. Examination of the last column of Table I reveals that as the yield of boric acid approaches the theoretical maximum, the average degree of hydroxylation falls steadily behind its

Table I. Yield of Boric Acid and Degree of Cage Hydroxylation

Hydroxyl equiv of MnO_4^-/mol of $B_{12}H_{12}^{2-}$	Theoret yield of $B(OH)_3$ in eq 1, % of $B_{12}H_{12}^{2-}$	Exptl yield of $B(OH)_3$, % of $B_{12}H_{12}^{2-}$	Av deg of hydroxyl, n_{av} in eq 2
1	4	0.51 ± 0.05	0.9
2	8	1.24 ± 0.07	1.7
3	12	2.70 ± 0.03	2.4
4	16	5.00 ± 0.50	2.9
5	20	7.25 ± 0.25	3.4
6	24	10.5 ± 0.8	3.8
7	28	13.9 ± 1.3	4.1
8	32	18.2 ± 1.4	4.2
9	36	22.5 ± 1.3	4.3
10	40	27.4 ± 1.4	4.4
11	44	32.0 ± 2.0	4.4
12	48	36.7 ± 1.8	4.4
15	60	51.2 ± 2.1	4.5
20	80	75.5 ± 2.4	4.6
25	100	97 ± 2.2	

theoretical value based on the number of hydroxylation equivalents of $KMnO_4$ added, and the n_{av} after rising sharply levels off at about 4.5.

This leveling and the fact that the number of tlc spots for the precipitated Cs^+ salts does not increase beyond 7 suggest a very simple degradation scheme. Addition of n_0 equivalents of $KMnO_4$ to $B_{12}H_{12}^{2-}$ produces a mixture of derivatives in which the number of hydroxyl groups per cage varies from 0 to a certain maximum value. The maximum depends on the reaction conditions, primarily the oxidation potential of the oxidizing agent, and any attempt to oxidize further the species results in breakup of the cage and rapid decomposition to boric acid. The boric acid thus would represent the fraction of $B_{12}H_{12}^{2-}$ that was pushed "over the brink." The fact that the average value of n levels off at 4.5 suggests that the breakup cannot occur at the pentahydroxy stage. At the same time the fact that no more than seven spots, some of which might even represent isomers, were ever seen on our tlc plates makes it unlikely that species having more than six hydroxy groups per cage have been isolated. Therefore, it would appear that either $B_{12}H_7(OH)_5^{2-}$ or $B_{12}H_6(OH)_6^{2-}$ is the most extensively substituted species capable of surviving under our experimental conditions. The latter seems a more likely candidate, since the hexahydroxy derivative produced in an exhaustive oxidation by a rather feeble oxidizing agent, *tert*-butyl alcohol, survived a reaction with elemental bromine and was isolated as $Cs_2B_{12}H_6Br_6$.[3] Since the pH of our solutions slowly rises from 7 to about 10, the standard reduction potential of the MnO_4^-–MnO_2 couple falls off from 1.140 to 0.903 V, spanning the reduction potential of Br_2 which is 1.066 V. At the concentrations used in our reactions the actual reduction potential of MnO_4^- should be only slightly below the standard value.

It is quite likely that the oxidation of $B_{10}H_{10}^{2-}$ proceeds in a similar fashion but the breakup should occur after fewer hydroxy groups are added, which might account for the faster formation of boric acid. Both $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ reduce $Cr_2O_7^{2-}$ to $Cr(OH)_2$ in neutral solutions without any evidence of oxidative coupling. The formation of $B_{12}H_{11}OH^{2-}$, indicated by the tlc of the reaction mixture and the ir spectrum of the double salt precipitated with CsCl, suggests that the oxidation mechanism is similar to that proposed for MnO_4^- though the rate is much slower.

A complete elucidation of the mechanism will require a kinetic study of two rapid steps in the reaction. The first is the introduction of hydroxy groups on a polyhedral cage. The mechanism might be similar to that postulated[4] for the reaction of olefins with alkaline $KMnO_4$ which yields diols. The second rapid reaction, which probably consists of a number of complicated steps, is the transition from a polyhydroxy ion to boric acid without evolution of hydrogen gas.

Experimental Section

Reagents and Instruments. Solutions of NaOH and $KMnO_4$ were prepared from reagent grade chemicals and standardized in the usual manner.[5] Solutions of $Na_2B_{12}H_{12}$, which was obtained from E. I. du Pont de Nemours and Co., were standardized by titration with NaOH after passage through an acid ion exchanger. Two solutions of $KMnO_4$, 0.1887 and 0.2080 M, and two of $Na_2B_{12}H_{12}$, 0.1131 and 0.1045 M, were used in our work. The tlc work was done on "Bakerflex" PEI-F impregnated cellulose on polyethylene sheets. The most satisfactory eluent contained acetonitrile, saturated aqueous $NaPF_6$, methanol, and water (20:17:2:1). The compounds were detected with 2% aqueous acidic $PdCl_2$. The ir spectra were recorded on a Perkin-Elmer Model 237B spectrophotometer. The ^{11}B nmr spectra were recorded on a Varian XL-100-15 spectrometer.

Boric Acid Determination. To 10 ml of 0.1131 M $Na_2B_{12}H_{12}$ (1.131 mmol) 3.99 ml of 0.1887 M $KMnO_4$ (0.753 mmol) was added *via* a microburet. The solution was stirred until all pink color disappeared and filtered through a sintered-disk funnel. The MnO_2 was washed with six 5-ml aliquots of water and the washings were combined with the filtrate. The filtrate was passed through an acid ion exchange column, neutralized with CsOH(aq), and concentrated by rotary evaporation to 20 ml. Addition of 20–30 ml of ethanol precipitated Cs^+ salts of polyhedral ions which were removed by filtration and saved. The boric acid content of the filtrate was determined by the conventional titration with NaOH in the presence of mannitol.[5] The same procedure was repeated with a series of solutions each containing a fixed amount of $Na_2B_{12}H_{12}$ and progressively more $KMnO_4$. The results are tabulated in Table I as per cent of $B_{12}H_{12}^{2-}$ converted to boric acid.

Polyhydroxy Derivatives. The solid salted out by ethanol prior to boric acid determination was dried *in vacuo* over P_2O_5 for 24 hr and its ir spectrum recorded. The spectrum was compared with those of $Cs_2B_{12}H_{12}$, $Cs_2B_{12}H_{11}OH$, and $Cs_2B_{12}H_{10}(OH)_2$; the last two were prepared by the pyrrolidone method.[3] Except for some very weak ones, all of the bands[3] belonging to the three ions listed above could be seen in the spectrum of our solid. Individual bands belonging to $B_{12}H_{11}OH^{2-}$ and $B_{12}H_{10}(OH)_2^{2-}$ could also be clearly distinguished in the solids precipitated from solutions to which less than 4 equiv of $KMnO_4$ had been added. When 4 equiv was added, most of the peaks in the fingerprint region coalesced into three very broad bands (with shoulders) at 1150 (s), 1030 (vs), and 840 (w) cm^{-1}. As more $KMnO_4$ was added, the band at 1150 cm^{-1} surpassed that at 1030 cm^{-1} in intensity, though both remained much more intense than that at 840 cm^{-1}; at the same time the 1030-cm^{-1} band shifted to lower frequencies (1015 cm^{-1} at 8 equiv). With increasing $KMnO_4$:$Na_2B_{12}H_{12}$ ratio the sharp O–H band at 3550 cm^{-1} coalesced with the broad band at 3350 cm^{-1} and the combined size of the two OH bands increased perceptibly in relation to the B–H bands at 2470–2500 cm^{-1}.

The tlc of the solid obtained with 1 equiv of $KMnO_4$ distinguished three spots of R_f 0.28, 0.40, and 0.48. These spots coincided with the positions occupied by $B_{12}H_{12}^{2-}$, $B_{12}H_{11}OH^{2-}$, and $B_{12}H_{10}(OH)_2^{2-}$, respectively, when the latter three were eluted alongside. When 2 or 3 equiv of $KMnO_4$ were used, a fourth spot appeared at R_f 0.54. By 5 equiv two additional spots appeared at R_f 0.60 and 0.66. From 6 equiv on, seven spots could be distinguished on the plates, with the highest at 0.70.

Isolation of $B_{12}H_{11}OH^{2-}$. Addition of concentrated aqueous CsCl to the first filtrate from any of the reactions (after the removal of MnO_2) precipitated a white solid which was shown to consist of the expected double salts $CsCl \cdot Cs_2B_{12}H_{11}OH$ and $CsCl \cdot Cs_2B_{12}H_{12}$ by examination of its ir, ^{11}B nmr, and tlc characteristics. The ir spectrum was free of any bands not attributable to the species in question and exhibited the characteristic band splitting associated with such double salts.[6] The ^{11}B nmr in water had a singlet and two overlapping doublets at the same positions as were seen in the spectrum of an authentic mixture of the two species.[3,6] The tlc contained only the two lowest spots at R_f 0.28 and 0.40. Conversion of the double salts to the corresponding Me_4N^+ salts followed by fractional crystallization from aqueous ethanol makes it possible to separate the less soluble $(Me_4N)_2B_{12}H_{12}$ from the $(Me_4N)_2B_{12}H_{11}OH$.

Reaction with $Na_2Cr_2O_7$. About 1 g of $Na_2Cr_2O_7 \cdot 2H_2O$ was dissolved in 10 ml of 0.10 *M* $Na_2B_{12}H_{12}$, and the reaction mixture stirred for 3 days at room temperature. Removal of the precipitated brown $Cr(OH)_2$ by filtration left a clear filtrate the tlc of which indicated the presence of $B_{12}H_{11}OH^{2-}$ in addition to the starting material, but no spots were seen corresponding to the positions occupied by $B_{24}H_{23}^{3-}$ or the $B_{24}H_{22}OH^{3-}$ species.[7,8] Addition of CsCl precipitated a mixture of $CsCl \cdot Cs_2B_{12}H_{12}$ and $CsCl \cdot Cs_2B_{12}H_{11}OH$. The ir spectra of precipitates obtained with either Cs^+ or Me_4N^+ showed no trace of the hydrogen-bridge band at 2270 cm^{-1} characteristic of the coupled ions.[7,8] The tlc and ir and uv spectra of salts precipitated by Cs^+ when dichromate was reduced by $B_{10}H_{10}^{2-}$ showed no evidence of $B_{20}H_{18}^{2-}$, $B_{20}H_{18}^{4-}$, or $B_{20}H_{17}OH^{4-}$. The ir spectra of Me_4N^+ salts reprecipitated from acidic solutions showed no evidence of $B_{20}H_{19}^{3-}$ or $B_{20}H_{18}OH^{3-}$ species.[9] The reduction of the dichromate proceeds much faster under reflux conditions.

Registry No. $B_{12}H_{12}^{2-}$, 12356-13-7; MnO_4^-, 14333-13-2.

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Behavior of Dieneiron Tricarbonyl Complexes in Strong Acid. Structures of the Protonated Species

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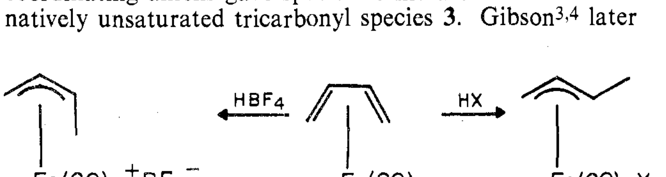
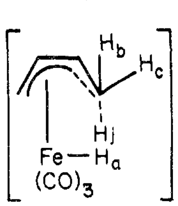
Received August 5, 1974 AIC40535F

A wide range of behavior has been reported for diene–metal complexes in acidic media. In early work,[1,2] addition of acids such as HCl to dieneiron tricarbonyl complexes **1** was observed to give π-allyliron carbonyl halides **2**, while acids with poorly coordinating anions gave species formulated as the coordinatively unsaturated tricarbonyl species **3**. Gibson[3,4] later reported the isolation from acetic acid–HBF_4 of π-allyl tetracarbonyl species **4**, which resulted presumably from capture of CO by species **3**. We observed similar behavior[5,6] in trifluoroacetic acid (TFA) and have discussed some mechanistic aspects of the protonation reaction. In SO_2, Kaesz, *et al.*,[7] have reported that diprotonated species, formulated as having structure **5**, are formed from **3** with excess strong acid. This species shows rather curious behavior, in that proton H_j was suggested to exchange rapidly with excess acid, while protons H_a, H_b, and H_c undergo rapid (nmr time scale at −20°) intramolecular scrambling. Similar observations have been made by Lewis[8] on (π-cyclohexadiene)(π-cyclopentadienyl)rhodium(I) in TFA solutions. Brookhart[9] has recently suggested that species **5** is actually better written as a σ–π species, **6**, and that the initial compound (1 equiv of acid) in SO_2 is actually analogous to **2**, with the anion of the acid coordinated to iron. We wish to report experimental evidence that this hypothesis is in fact the case and that the species **6**, formed on treatment with excess HBF_4, is monoprotonated.

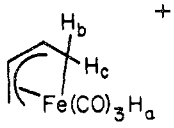


3 **1** **2**

4



5



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Experimental Section

General Data. All reactions involving organometallics were performed under an atmosphere of dry nitrogen, and nmr samples were likewise prepared under nitrogen. Silver trifluoroacetate[10] and η-allyliron tricarbonyl iodide[11] were prepared by known methods. Proton nmr spectra were obtained on a JEOL Model JNM-MH-100 spectrometer operating on external lock, at ambient temperature (~31°). Conductivity measurements were performed using a Beckman Model RC-18A conductivity bridge at 31°. Solutions of anhydrous HBF_4 in TFA were made by the addition of a known quantity of 40% aqueous HBF_4 to a slight excess of trifluoroacetic anhydride, followed by dilution to the appropriate concentration with TFA.

(1-Phenyl-3-methylbutadiene)iron Tricarbonyl (7). 1-Phenyl-3-methylbutadiene[12] was prepared from benzalacetone by reaction with methylmagnesium bromide and dehydration. The complex was prepared by irradiation of a solution of 9.0 g (0.063 mol) of the diene and 7.84 g (0.040 mol) of iron pentacarbonyl in 75 ml of benzene contained in an annular photolysis well with a Hanovia 450-W medium-pressure mercury arc for 5 hr. The resulting solution was transferred out of the well with the aid of 25 ml of benzene and filtered, and the solvent and excess iron pentacarbonyl were removed by evaporation under reduced pressure. Distillation gave 9.82 g of yellow oil, bp 60–110° (0.005 mm), which crystallized on standing. Recrystallization from pentane, followed by sublimation (45°, 0.005 mm) gave 6.2 g (50%) of yellow crystalline material, mp 42–44°.

Anal. Calcd for $C_{14}H_{12}FeO_3$: C, 59.15; H, 4.26; Fe, 19.69. Found: C, 59.36; H, 4.44; Fe, 19.87.

(1-Phenyl-3,3-dimethylallyl)iron Tetracarbonyl Tetrafluoroborate (9). Carbon monoxide was bubbled into a solution of 5.68 g (20 mmol) of the above diene complex in 20 ml of TFA for 15 min. A solution of 20 mmol of HBF_4 in 25 ml of TFA was added, and the solution was allowed to stand a further 15 min under a vigorous stream of CO. The resulting solution was poured into 75 ml of ether, and the resulting yellow precipitate was filtered, washed with ether, and dried under a stream of nitrogen. It was then redissolved in a minimum volume of TFA and reprecipitated by the addition of ether. Filtration, followed by drying under vacuum for 8 hr at 50°, gave 6.3 g (78%) of yellow powder. Ir (CH_3NO_2): 2130 (s), 2080–2050 cm^{-1} (br, s) (ν_{CO}). Nmr (TFA): δ 2.00 (s, 3 H), 2.40 (s, 3 H), 5.52 (d, *J* = 13 Hz, 1 H), 6.45 (d, *J* = 13 Hz, 1 H), *ca.* 7.5 (m, 5 H).

Anal. Calcd for $C_{15}H_{13}FeO_4BF_4$: C, 45.05; H, 3.28; Fe, 13.96. Found: C, 44.76; H, 3.50; Fe, 13.83.

Allyliron Tetracarbonyl Tetrafluoroborate. Allyliron tricarbonyl iodide (1.54 g, 5 mmol) and $AgBF_4$ (1.17 g, 6 mmol) were dissolved in 10 ml of TFA. Carbon monoxide was bubbled rapidly through