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COMPOUNDS CONSISTING OF HYDROCARBON GROUPS AND ALUMINUM AND/OR BORON ATOMS

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This invention relates to new chemical compositions containing boron and/or aluminum, which are particularly useful as high energy fuels. It also relates to methods of preparing such compositions. More specifically, it relates to boron and/or aluminum hydrocarbon compounds containing a plurality of such metal atoms.

Alkyl boron and alkyl aluminum compounds have been found desirable for use as liquid fuels for propelling missiles, rockets, etc. In order to have a maximum energy content, the hydrocarbon portion of such compounds should represent as low a proportion as possible of the total weight. However, the presently known alkyl borons and alkyl aluminums having the desired high energy for such purposes are low boiling and have high volatility and toxicity. Attempts to decrease the boiling point and volatility by increasing the size or length of the alkyl groups attached to the metal result in a lower proportion of metal in the compounds and, therefore, a lower energy content.

In accordance with the present invention, new metallo-hydrocarbon compounds containing a plurality of boron and/or aluminum atoms have been found which have higher boiling points and lower volatility, and thereby reduce the tendency to cause toxicity and eliminate the necessity for use under pressure. These new compounds have a high proportion of metal therein, and, therefore, have as high or even higher energy content that is utilizable for propellant purposes than the presently known alkyl boron or aluminum compounds. These compounds contain at least four atoms of metal therein and are represented by the formula

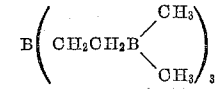
$$M[CR_2—(CR_2)_m—MR'_2]_3$$

wherein M is boron or aluminum, R is preferably hydrogen but also can be a hydrocarbon group as defined for R' and said R can have on one of said hydrocarbon groups one or more other MR'_2 groups, preferably BR'_2; R' is a hydrocarbon group of no more than 8 carbon atoms, preferably no more than 3, and *m* is an integer having a value of at least 1 and no more than 8, preferably no more than 4. Generally the advantages of this invention are realized when the number of MR'_2 groups in a compound are no more than ten.

One advantage of boron compounds over aluminum compounds for use in rocket and missile fuels is the lower atomic weight of boron as compared to aluminum. The atomic weight of boron is approximately 11 and that for aluminum is approximately 27. Therefore, for corresponding types of compounds, a given weight of the boron compound will contain a greater number of boron atoms than the number of aluminum atoms contained in a corresponding weight of the aluminum compounds. Thus,

in rockets and missiles where the amount of energy derived per unit weight of fuel is very critical and the fuel consists of compounds having high proportions of metal therein, the boron compounds have a decided advantage. In the compounds of this invention where at least four boron atoms are contained in each molecule, this advantage is even more emphasized. In those compounds in which there are one or more aluminum atoms, the higher atomic weight of the aluminum atom is offset to some extent by the fact that there are a plurality of metal atoms per molecule, and the ratio of metal to hydrocarbon portions generally compensates for the higher atomic weight of aluminum.

A comparison of trimethyl boron with one of the simplest compounds of this invention, namely tris- beta-(dimethyl boro)-ethyl -borane,



can illustrate the advantage cited above. The latter compound has an empirical formula of $B_4C_{12}H_{30}$ and can be regarded as having $C_3H_{7.5}$ per boron atom. In comparison, trimethyl boron has an empirical formula of BC_3H_9, and while it has the same number of carbon atoms per boron atom, it actually has 1.5 hydrogen atoms more per boron atom than the new compound described above. However, trimethyl boron is a gas at room temperature, having a boiling point of −20° C., must be used as a liquefied compressed gas, and is very toxic. In contrast, the new compound described above has a much higher boiling point and relatively low volatility, therefore involving less danger with respect to toxicity, and can be used without pressure.

A simple preferred method for preparing compounds of this invention is by the addition of boron hydride or aluminum hydride to a boron or an aluminum compound having three hydrocarbon groups attached thereto, one of which hydrocarbon groups is an alkenyl group, for example vinyl-dimethyl-boron or vinyl-dimethyl-aluminum.

As an alternate synthesis, these compounds also can be prepared by reacting an aluminum hydride or a boron hydride compound having two hydrocarbon groups attached to the boron or aluminum, which hydrocarbon groups have no ethylenic unsaturation therein, with an unsaturated compound of the structure

$$[CR_2=CR(CR_2)_{m-1}]_3M$$

wherein R, M, and *m* are as defined above.

The above reactions can be represented as:

$$MH_3+3CR_2=CR-(CR_2)_{m-1}—MR'_2\rightarrow M[—CR_2(CR_2)_m—MR'_2]_3$$

$$3R'_2MH+[CR_2=CR-(CR_2)_{m-1}]_3M\rightarrow [R'_2M(CR_2)_mCR_2—]_3M$$

These reactions are catalyzed by an ether compound, such as diethyl ether, tetrahydrofurane, diglyme, etc., as well as boron or aluminum compounds containing hydrocarbon and ether groups therein, such as, for example, (vinyloxy-ethyl)-dimethyl boron, (vinyloxy-ethyl)-diethyl boron, ethyl-bis-(ethoxy-ethyl)-boron, tris-(ethoxy-ethyl)-boron, (vinyloxy-ethyl)-dimethyl aluminum, (vinyloxy-ethyl)-diethyl aluminum, ethyl-bis-(ethoxy-ethyl)-aluminum, tris-(ethoxy-ethyl)-aluminum, etc.

Traces of the ether compounds are sufficient to catalyze reaction markedly. Therefore, the ether is used advantageously in minor amounts and, unless it is also to be used as a solvent or suspension medium, there is no need for more than 5 percent required for catalytic purposes. Also, as catalysts for the reaction of this invention, various compounds of the formulas $B(OR'')_3$ and $Al(OR'')_3$ can be used, in which R'' is hydrogen or a monovalent hydrocarbon group of the types indicated above, with at least one R'' in each compound being such a hydrocarbon group. Typical examples of such compounds include: trimethyl borate, dimethyl borate, methyl borate, tripropyl borate, dibutyl borate, monoamyl borate, dioctyl borate, monophenyl borate, dibenzyl borate, tricyclohexyl borate, triphenethyl borate, etc., and the corresponding aluminates, such as triethyl aluminate, propyl aluminate, benzyl aluminate, diphenethyl aluminate, cyclohexyl aluminate, etc.

As discussed more fully hereinafter, the reaction desirably is maintained at such a temperature that the hydride reacts only to the extent that there is hydrogen on the metal atom, and not high enough to replace any hydrocarbon groups thereon. While the compounds of this invention can be produced to some extent by the first of the above methods also by starting with boron or aluminum compounds having three saturated hydrocarbon groups attached to the metal atom, or more than one hydrogen atom attached to the metal atom, such reactions are more difficult to control and considerable amounts of more highly substituted byproduct materials are produced, generally of a polymeric nature.

The addition reactions advantageously are conducted in the absence of moisture, or air, so as to prevent decomposition of the starting materials and products. Inert atmospheres and inert diluents advantageously are used. Nitrogen, argon, gaseous hydrocarbons, such as methane, ethane, etc., are used advantageously as inert atmospheres, and saturated hydrocarbons, such as pentanes, hexanes, heptanes, cyclohexanes, and even aromatic hydrocarbons, such as benzene, toluene, etc., are used advantageously as diluents.

Unsaturated compounds that can be used as intermediates in preparing the compounds of this invention by the first of the above methods can be represented by the formula

$$CR_2{=}CR{-}(CR_2)_{m-1}{-}MR'_2$$

wherein R, R', M, and *m* are as defined above. Compounds having a terminal ethylenic group, i.e. a terminal vinyl or vinylidene group, are preferred. Typical examples of such compounds include, but are not restricted to, the following:

vinyl-dimethyly-boron,
vinyl-diethyl-boron,
vinyl-dipropyl-boron,
vinyl-dibutyl-boron,
vinyl-diamyl-boron,
vinyl-diphenyl-boron,
vinyl-dicyclohexyl-boron,
vinyl-methyl-ethyl-boron,
vinyl-ethyl-propyl-boron,
vinyl-methyl-phenyl-boron,
vinyl-ethyl-cyclohexyl-boron,
allyl-dimethyl-boron,
allyl-diethyl-boron,
allyl-dipropyl-boron,
allyl-dibutyl-boron,
allyl-ditolyl-boron,
allyl-dicyclopentyl-boron,
isopropenyl-dimethyl-boron,
isopropenyl-diethyl-boron,
isopropenyl-dipropyl-boron,
isopropenyl-dibutyl-boron,
isopropenyl-methyl-ethyl-boron,
isopropenyl-ethyl-propyl-boron,
isopropenyl-dixylyl-boron,
beta-vinyl-triethyl-boron,
(beta-vinyl-ethyl)-dimethyl-boron,
(betal-vinyl-ethyl)-dipropyl-boron,
isobutenyl-dibutyl-boron,
(4-vinyl-cyclohexyl)-dimethyl-boron,
(4-vinyl-n-butyl)-diethyl-boron,
(6-vinyl-n-hexyl)-dimethyl-boron,
vinyl-dimethyl-aluminum,
vinyl-diethyl-aluminum,
vinyl-dipropyl-aluminum,
vinyl-dibutyl-aluminum,
vinyl-diamyl-aluminum,
vinyl-diphenyl-aluminum,
vinyl-dicyclohexyl-aluminum,
vinyl-methyl-ethyl-aluminum,
vinyl-ethyl-propyl-aluminum,
vinyl-methyl-phenyl-aluminum,
vinyl-ethyl-cyclohexyl-aluminum,
allyl-dimethyl-aluminum,
allyl-diethyl-aluminum,
allyl-dipropyl-aluminum,
allyl-dibutyl-aluminum,
allyl-ditolyl-aluminum,
allyl-dicyclopentyl-aluminum,
isopropenyl-dimethyl-aluminum,
isopropenyl-diethyl-aluminum,
isopropenyl-dipropyl-aluminum,
isopropenyl-dibutyl-aluminum,
isopropenyl-methyl-ethyl-aluminum,
isopropenyl-ethyl-propyl-aluminum,
isopropenyl-dixylyl-aluminum,
beta-vinyl-triethyl-aluminum,
(beta-vinyl-ethyl)-dimethyl-aluminum,
(beta-vinyl-ethyl)-dipropyl-aluminum,
isobutenyl-dibutyl-aluminum,
(4-vinyl-cyclohexyl)-dimethyl-aluminum,
(4-vinyl-n-butyl)-diethyl-aluminum,
(6-vinyl-n-hexyl)-dimethyl-aluminum,
crotyl-dimethyl-boron,
crotyl-diethyl-boron,
crotyl-dipropyl-aluminum, etc.

Such intermediate compounds as listed in the preceding paragraph can be prepared according to well-known, standard reactions of dialkll boron halides and dialkyl aluminum halides with appropriate Grignard reagents, such as vinyl magnesium chloride, allyl magnesium bromide, etc., or by reaction of these same halides with divinyl tin, tetravinyl lead, etc. Such reactions are illustrated as follows:

$$CH_2{=}CHCl + Mg \xrightarrow[\text{Tetrahydrofurane}]{} CH_2{=}CHMgCl$$

$$CH_2{=}CHMgCl + R'_2BCl \longrightarrow CH_2{=}CHBR'_2 + MgCl_2$$

$$CH_2{=}CHMgCl + R'_2AlCl \longrightarrow CH_2{=}CHAlR'_2 + MgCl_2$$

Such reactions can be represented by the following general reaction:

$$CR_2{=}CR(CR_2)_{m-1}Cl + Mg \longrightarrow CR_2{=}CR(CR_2)_{m-1}MgCl$$

$$\downarrow R'_2MCl$$

$$CR_2{=}CR(CR_2)_{m-1}MR'_2$$

wherein R, M, R', and *m* are as defined above.

Preparation from alkenyl tin and alkenyl lead starting compounds are also typified by the following reactions:

$$(CH_2{=}CH)_2Sn + 2R'_2BCl \rightarrow 2CH_2{=}CHBR'_2 + SnCl_2$$

$$(CH_2{=}CH{-}CH_2)_2Sn + 2R'AlCl \rightarrow 2CH_2{=}CHCH_2AlR'_2 + SnCl_2$$

$$(CH_2{=}CHCH_2)_4Pb + 4R'BCl \rightarrow 4CH_2{=}CHCH_2BR'_2 + PbCl_4$$

$$(CH_2{=}CH)_4Pb + 4R'AlCl \rightarrow 4CH_2{=}CHAlR'_2 + PbCl_4$$

Such intermediate compounds also can be prepared by the reaction of dialkyl boron hydrides and dialkyl alu-

minum hydrides, or corresponding compounds having aryl or cycloaliphatic hydrocarbon groups in place of the alkyl groups, with a considerable excess of an acetylenic or diolefinic hydrocarbon, in such a manner, for example by controlling the temperature and time of reaction, that the metal hydrides react only to the extent that there is hydrogen attached to the metal atom in the compound and that the acetylenic or diolefinic material reacts only to the extent of half of the unsaturation therein, e.g.

$$CH_2=CH-CH=CH_2+R'_2BH\rightarrow CH_2=CHCH_2CH_2BR'_2$$
$$HC\equiv CH+R'_2BH\rightarrow CH_2=CH-BR'_2$$
$$CH_2=C=CH_2+R'_2BH\rightarrow CH_2=CHCH_2BR'_2$$

etc. Corresponding reactions can be performed with R'_2AlH to give the corresponding intermediates. These intermediates are then further reacted in accordance with the practice of this invention.

It is preferred for two reasons that the R' groups of the metal hydrides be small aliphatic groups. First, the use of smaller groups results in a higher proportion of metal in the resulting compounds. Secondly, the larger bulky groups retard somewhat the addition of the metal compounds to the unsaturated compounds, thereby necessitating more drastic reaction conditions and longer reaction periods. Therefore, methyl, ethyl, and propyl groups are preferred in place of the bulkier groups, such as phenyl, cyclohexyl, and aliphatic groups having groups attached to that carbon atom which will become attached to the metal atom, such as alpha, beta-dimethyl-propyl, etc.

The above reaction for preparation of the intermediates can be controlled by using an excess of the unsaturated material over the stoichiometric amount required (mole of hydride per mole of unsaturated compound) and by maintaining a reaction temperature which will favor reaction to the extent that there is hydrogen present in the metal compounds, which temperature should be below the temperature which will cause replacement of the hydrocarbon groups on the metal compound. This reaction also can be catalyzed by the ethers and other compounds indicated above.

Typical metal compounds that can be used as starting materials in preparing the compounds of this invention by the first of the above-described methods include, but not restricted to, the following: dimethyl boron hydride, diethyl boron hydride, dipropyl boron hydride, dibutyl boron hydride, diphenyl boron hydride, diphenethyl boron hydride, dicyclohexyl boron hydride, di-(cyclohexylethyl)-boron hydride, dimethyl aluminum hydride, diethyl aluminum hydride, dipropyl aluminum hydride, dibutyl aluminum hydride, diphenyl aluminum hydride, dipentyl aluminum hydride, diphenethyl aluminum hydride, dicyclohexyl aluminum hydride, di-(cyclohexylethyl)-aluminum hydride, etc. In some cases, where such compounds are difficult to prepare or are unstable, the polymeric counterparts of such compounds which give the same addition derivatives as the monomeric materials can be used, such as, for example, tetramethyl diborane, hexamethyl triborane, tetraethyl diborane, tetramethyl dialuane, tetraethyl dialuane, etc. In addition various mixed hydrocarbon compounds also can be used, such as, for example, methyl ethyl boron hydride, ethyl propyl aluminum hydride, methyl propyl aluminum hydride, ethyl butyl boron hydride, etc.

The optimum temperature for effecting the addition reaction depends on a member of factors. The use of a catalyst, such as an ether compound, as listed above, permits the addition to take place at room temperature or only slightly raised temperatures. In the absence of a catalyst, higher temperatures are required. However, the use of a catalyst is preferred so as to avoid formation of byproducts which accompanies the use of higher temperatures.

The type of unsaturated group in the hydrocarbon also influences the ease of addition and, therefore, the temperature required to effect the same. For example, terminal ethylenic groups, such as vinyl, vinylidene, and propargyl groups permit additions at lower temperatures than is the case with non-terminal ethylenic groups. Generally, in cases which require higher temperatures to effect the hydride addition, the same factors cause a corresponding increase in the temperature which will effect replacement of hydrocarbon groups from the metal atoms.

Also, as a general rule, the addition of boron hydride compounds requires a lower temperature than the corresponding addition of aluminum hydride compounds. For that reason, it is generally advantageous to effect the aluminum hydride compound addition prior to the addition of the boron hydride compound, lowering the temperature after the first addition, so that the temperature used in the aluminum addition will not cause displacement of the hydrocarbon groups in the boron compound. In the aforesaid preliminary step of aluminum addition, an excess of the hydrocarbon can be used to retard any formation of dialuminum compounds. This excess of hydrocarbon can be removed prior to the boron addition by the application of reduced pressure, or, if the presence of diboron products are not objectionable, an appropriate amount of the boron compound can be used to make the mixed boron-aluminum compound and an amount of diboron compound corresponding to the excess hydrocarbon compound used.

In cases where the boron compound is to be added first, a temperature will be selected for the aluminum compound addition that is below the temperature which will effect hydrocarbon displacement from the boron atom. In such cases, longer reaction times can be used to compensate when the selected temperature is lower than is used ordinarily for such aluminum addition.

In the absence of a catalyst, the addition of the aluminum compound can be effected easily at temperatures in the range of 90°–95° C. With ethers, and other types of catalysts, the addition can be effected at temperatures of 70°–80° C. or even lower. Temperatures even below 50° C. can be used by using the catalyst indicated and longer reaction periods. It is preferred to keep the temperature below 100° C. to avoid displacement of the hydrocarbon groups from the aluminum.

With the boron compound, it is possible to effect the addition to the unsaturated hydrocarbon group at temperatures below 40° C. and with the catalysts indicated, it is possible to effect the addition at room temperature or at even lower temperatures. In some cases, temperatures above 50° C. may favor displacement of the hydrocarbon groups from the boron.

Unsaturated compounds that can be used as intermediates in preparing compounds of this invention by the second method described above are the various trialkenyl boron and aluminum compounds of the formulas indicated. Compounds having a terminal ethylenic group, e.g. a vinyl or vinylidene group are preferred. Typical examples of compounds that can be used include, but are not restricted to, the following: trivinyl boron, triallyl boron, tri-isopropenyl boron, tris-(beta-vinyl-ethyl)-boron, tris-(4-vinyl-n-butyl)-boron, tris-(6-vinyl-n-hexyl)-boron, tricrotyl boron, divinyl-allyl-boron, divinyl-isopropenyl-boron, divinyl-(4-vinyl-n-butyl)-boron, divinyl-(beta-vinyl-ethyl)-boron, divinyl-crotyl-boron, allyl-diisopropenyl-boron, diallyl-isopropenyl-boron, diallyl-crotyl-boron, diallyl-(4-vinyl-n-butyl)-boron, isopropenyl-di-(4-vinyl-n-butyl)-boron, diisopropenyl-(2-vinyl-ethyl)-boron, trivinyl aluminum, triallyl aluminum, tri-isopropenyl aluminum, tris-(beta-vinyl-ethyl)-aluminum, tris-(4-vinyl-n-butyl)-aluminum, tris-(6-vinyl-n-hexyl)-aluminum, tricrotyl aluminum, divinyl-allyl-aluminum, divinyl-isopropenyl-aluminum, divinyl-(4-vinyl-n-butyl)-aluminum, divinyl-(beta-vinyl-ethyl)-aluminum, divinyl-crotyl-aluminum, allyl-diisopropenyl-aluminum, diallyl-isopropenyl-aluminum, diallyl-crotyl-aluminum, diallyl-(4-vinyl-n-butyl)-aluminum, isopropenyl-di-(4-vinyl-n-butyl)-aluminum, diisopropenyl-(2-vinyl-ethyl)-aluminum, etc.

Such intermediate compounds as listed in the preceding paragraph can be prepared according to well-known, standard reactions, using boron trihalides and aluminum trihalides with appropriate Grignard reagents, such as vinyl magnesium chloride, allyl magnesium bromide, etc., or by reaction of the same halides with divinyl tin, tetravinyl tin, etc. Such reactions are illustrated as follows:

$$3CH_2{=}CHMgCl + BCl_3 \rightarrow (CH_2{=}CH)_3B + 3MgCl_2$$

$$3CH_2{=}CHCH_2MgCl + AlCl_3 \rightarrow (CH_2{=}CHCH_2)_3Al + 3MgCl_2$$

Such reactions can be represented by the following general reaction:

$$3CR_2{=}CR(CR_2)_{m-1}MgCl + MCl_3 \rightarrow [CR_2{=}CR(CR_2)_{m-1}]_3M + 3MgCl_2$$

wherein R, M, R', and *m* are as defined above.

Preparation from alkenyl tin and alkenyl lead starting compounds are typified by the following reactions:

$$3(CH_2{=}CH)_2Sn + 2BCl_3 \rightarrow 2(CH_2{=}CH)_3B + 3SnCl_2$$

$$3(CH_2{=}CHCH_2)_2Sn + 2AlCl_3 \rightarrow 2(CH_2{=}CHCH_2)_3Al + 3SnCl_2$$

$$3(CH_2{=}CHCH_2)_4Pb + 4BCl_3 \rightarrow 4(CH_2{=}CHCH_2)_3B + 3PbCl_4$$

$$3(CH_2{=}CH)_4Pb + 4AlCl_3 \rightarrow 4(CH_2{=}CH)_3Al + 3PbCl_4$$

Such intermediate compounds also can be prepared by the reaction of boron hydride and aluminum hydride with a considerable excess of an acetylenic or diolefinic hydrocarbon, in such a manner that the metal hydrides react with the acetylenic or diolefinic material only to the extent of half the unsaturation therein, e.g.

$$CH_2{=}CH{-}CH{=}CH_2 + BH_3 \rightarrow (CH_2{=}CHCH_2CH_2)_3B$$

$$HC{\equiv}CH + BH_3 \rightarrow (CH_2{=}CH)_3B$$

$$CH_2{=}C{=}CH_2 + R'_2BH \rightarrow (CH_2{=}CHCH_2)_3B$$

etc.

Generally an excess of ten moles of the unsaturated starting compound per mole of such compound required stoichiometrically is sufficient to prevent reaction of the metal hydride with the remaining unsaturation in the desired compound. Excess unsaturated reagent eventually is removed by lowering the temperature to prevent further condensation and applying reduced pressures to evaporate the unreacted unsaturated starting material. Corresponding reactions can be performed with aluminum hydride to give the corresponding intermediate. These intermediates are then further reacted in accordance with the practice of this invention.

In the type of reaction identified above as the second method of preparing the compounds of this invention, e.g. where boron hydride or aluminum hydride, as well as the various polymeric forms of these hydrides, such as diborane, dialuane, etc., are used, the conditions for the addition reaction are generally similar to those for the first type of reaction except that the addition is effected more easily and in most cases can be effected at temperatures lower than are required for the addition of the disubstituted metal hydride in the first type of reaction. Roughly, temperatures 20–30° C. lower than those used in the first type of reaction will give comparable rates of reaction when the corresponding unsubstituted metal hydride is used.

The new compounds of this invention are either liquids or solids. When it is desired to use the solid compounds of this invention in systems designed for high-energy liquid fuels, these compounds can be converted to liquids by dilution or dissolving in the simpler or lower melting compounds of this invention or various liquid alkyl boron or alkyl aluminum compounds so as to avoid lowering, no more than desirable or necessary, the proportion of metal in the fuel compositions.

Various methods of practicing the invention are illustrated by the following examples. The examples are intended merely to illustrate the invention, and not in any sense to limit the manner in which the invention can be practiced. The parts and percentages recited therein, and also in the specification, unless specifically provided otherwise, refer to parts by weight and percentages by weight.

Example I

A glass reaction vessel equipped with stirrer, reflux condenser, and gas inlet, is flushed out with oxygen-free nitrogen and an atmosphere of nitrogen maintained therein. A solution of 250 parts of diethyl ether and 206 parts of vinyl dimethyl borane is added to the reaction vessel and cooled to 0° C. (The vinyl dimethyl borane is prepared from dimethyl boron chloride and tetravinyl tin according to paper 69, page 26M, Abstract of Papers, 135th meeting American Chemical Society, April 5, 1959.) Diborane gas is fed into the reaction mixture at a rate such that 13.8 parts of diborane are absorbed over a period of approximately two hours. After the absorption is completed, the reaction mass is allowed to come to room temperature and the stirring continued for another eight hours. The greater part of the ether solvent is removed by distillation, the reaction mass temperature being maintained at no more than 40° C. Then, while the nitrogen atmosphere is still maintained in the system, the reaction product is transferred to distillation equipment provided with means for effecting distillation at reduced pressures. The pressure is reduced gradually to effect removal of the last traces of ether and unreacted reagents and the product isolated in the boiling range of 40°–80° C. at 0.1–0.5 mm.

Product analysis shows 19.6 percent boron which is in good agreement with the theoretical value for tris-(beta-dimethyl-boro-ethyl)-borane. Methane and ethane are given off upon decomposition with water.

The foregoing procedure is repeated except that an equivalent amount of AlH_3 is substituted for the diborane and is added in the form of an ether solution of the etherate, $3AlH_3 \cdot Et_2O$. The corresponding aluminum-boron compound is obtained, namely tris-(beta-dimethyl-boro-ethyl)-aluane.

Example II

The substitution of dimethyl allyl borane in a repetition of the procedure of Example I for the dimethyl vinyl borane produces the corresponding tris-(3-dimethyl-boro-propyl)-borane which is isolated in the boiling range of 50°–90° C. at 0.1 to 0.5 mm. The isolated product contains 16.4 percent boron, and methane and propane are given off upon decomposition with water.

Example III

The substitution of dimethyl allyl aluminum for the dimethyl allyl borane in a repetition of the procedure of Example II produces the corresponding aluminum compound, namely tris-(3-dimethyl-alumino-propyl)-borane, which is isolated in the boiling range of 55°–100° C. at 0.1 to 0.4 mm. Product analysis shows 4.7 percent boron and 28 percent aluminum, which values are in good agreement for the expected compound. Methane and propane are given off on decomposition of a sample of the product with water.

Example IV

The procedure of Example I is repeated using the same weight of diglyme instead of the ethyl ether, 82 parts of trivinyl borane (Chem. Rev., 56, 959–1056 (1956)), and 126 parts of tetramethyl diborane. The isolated product corresponds to that of Example I. When an equivalent weight of tetramethyl dialuane is substituted for the tetramethyl diborane and the above procedure is repeated using a temperature of 90° C. for the addition reaction, the aluminum and boron analyses of the product corresponds to the theoretical values for tris-[beta-(dimethyl aluminate)-ethyl]-borane.

Example V

The procedure of Example I is repeated, omitting the viny dimethyl borane and the diborane. Instead acetylene is bubbled into the ether until it is saturated and the saturated condition maintained during the reaction by continuously bubbling acetylene through the reaction solution. 378 parts of dibutyl boron are fed into the ether solution gradually over a period of two hours. After addition is completed, the reaction is continued for half an hour. Then, the acetylene supply is cut off and unreacted acetylene is removed by bubbling oxygen-free nitrogen through the solution for fifteen minutes. Diborane is then fed into the solution until four parts have been absorbed and the reaction continued for another half hour. The reaction product comprises tris-(beta-dibutyl-boro-ethyl)-borane, having the formula

$$B[CH_2CH_2B(C_4H_9)_2]_3$$

Example VI

The procedure of Example I is repeated at 70° C. using 30 parts of aluminum hydride and 240 parts of dimethyl allyl borane to give an excellent yield of

$$Al[CH_2CH_2CH_2B(CH_3)_2]_3$$

which is isolated by distillation at 50–100° C. at 0.1 to 0.6 mm. On decomposition with water the product gives off methane and propane. Substitution of an equivalent amount of dimethyl allyl aluminum for the dimethyl allyl borane in a repetition of this procedure produces the corresponding aluminum derivative, namely tris-(3-dimethyl-alumino-propyl)-aluane.

Example VII

In accordance with the procedure of Example V, a solution of 126 parts of tetramethyl diborane in 250 parts of diglyme is fed gradually into 250 parts of diglyme maintained at room temperature, under an atmosphere of nitrogen, and in a state of agitation, while the diglyme solution is maintained saturated with butadiene which is fed into the solution continuously. The agitation then is continued for an additional four hours. Then unreacted butadiene is removed by bubbling nitrogen through the solution for half an hour, after which 14 parts of diborone are passed into the reaction mass in the course of two hours. The pressure is then reduced gradually to remove solvent and unreacted reagent, and subsequently to recover the product. Ultimate analysis of the distilled product shows 14.2 percent borone, which checks closely with the theoretical value for boron in

$$B[CH_2CH_2CH_2CH_2B(CH_3)_2]_3$$

Repetition of the foregoing procedure with 2-phenyl butadiene in place of the butadiene gives the corresponding phenyl derivative, whereas isoprene gives the corresponding methyl derivative.

Example VIII

The procedure of Example VII is repeated except that vinyl acetylene is used instead of butadiene. Ultimate analysis of the distilled product shows a boron content of 17.95 percent, which is in fair agreement with the compound tris-[bis-(dimethyl-boro)-butyl]-borane.

It is also possible to use mixtures of the various types of reagents indicated above. For example, in the first type of reaction, the monoalkenyl reagent can comprise a mixture of two or more monoalkenyl compounds in which the alkenyl radical, the metal atom, or the R′ groups can each or all be different. As an illustration, a mixture of dimethyl vinyl borane and dimethyl vinyl aluane can be reacted with diborane to give a mixture of products in which the compounds contain 4 atoms of boron, 3 atoms of boron and 1 of aluminum, 2 atoms of boron and 2 of aluminum, and 1 atom of boron and 3 of aluminum, respectively. The proportions of these compounds in the product mixture and the relative proportions of metal atoms therein depend on the concentrations and the relative reactivity of the various reagents. Another illustration is to react a mixture of dimethyl vinyl borane and dimethyl allyl borane with diborane. Another variation is to react diborane with dimethyl vinyl borane and dimethyl allyl aluane. It is also possible to use mixtures of the metal hydrides, for example reacting a mixture of diborane and dialuane with dimethyl vinyl borane, diethyl allyl aluane, etc.

In the second type of reaction, it is also possible to use various mixtures of reagents, for example trivinyl borane can be reacted with a mixture of tetramethyl diborane and tetramethyl dialuane to give a mixture of products varying in the number of the different types of metal atoms therein. The hydrocarbon groups on the various metal reagents also can differ either in the same compound or in the different compounds in the mixture. Likewise, a mixture of the trialkenyl metal compounds also can be used. For example, two or more alkenyl metal compounds containing the same or the different metal atoms therein can be reacted with one or more of the di-substituted metal hydrides. For example, a mixture of trivinyl borane and trivinyl aluane can be reacted with tetramethyl diborane or tetramethyl dialuane, or a mixture of the di-substituted hydrides.

In some cases, particularly where the compositions are to be used for fuel purposes, the product mixtures can be used directly without separation of the various compounds. In other cases, the various constituent compounds can be separated by fractional distillation at reduced pressures. The ease of such separation depends on the comparative sizes of the various substituent groups in the compounds and resultant differences in boiling points of these products.

Using the procedure of the foregoing examples or appropriate modifications thereof with appropriate unsaturated compounds and appropriate metal hydrides, the following compounds typical of the compounds of this invention are prepared:

$B[CH_2CH_2B(C_2H_5)_2]_3$

$Al[CH_2CH_2B(C_2H_5)_2]_3$

$B[CH_2CH_2B(C_3H_7)_2]_3$

$B[CH_2CH_2B(C_2H_4C_6H_5)_2]_3$

$B[CH_2CH_2Al(CH_3)_2]_3$

$B[CH_2CH_2CH_2B(C_2H_5)_2]_3$

$B[CH_2CH_2CH_2Al(C_6H_5)_2]_3$

$Al[CH_2CH_2CH_2Al(C_4H_9)_2]_3$

$Al[CH_2CH_2Al(C_2H_5)_2]_3$

$Al[CH_2CH_2CH_2Al(C_3H_7)_2]_3$

$$B\left[CH_2CHB(CH_3)_2\right]_3 \qquad B\left[CHCH_2Al(C_2H_5)_2\right]_3$$
$$\quad\ CH_3 \qquad\qquad\qquad\quad CH_3$$

$B[CH_2CHCH_2CH_2B(CH_3)_2]_3$

$B[CH_2CH_2CH_2CH_2B(C_2H_5)_2]_3$

$$B\left[CH_2CHCH_2CH_2Al(C_2H_5)_2\right]_3 \qquad B\left[CH_2CHCH_2CH_2Al(CH_3)_2\right]_3$$
$$\quad\ C_6H_5 \qquad\qquad\qquad\qquad\quad CH_3$$

$$B\left[CH_2CH_2CH_2CHAl(CH_3)_2\right]_3$$
$$\quad\ CH_3$$

$Al[CH_2CH_2CH_2B(C_5H_{11})_2]_3$

$B[(CH_2)_8B(CH_3)_2]_3$

$B[(CH_2)_8Al(C_2H_5)_2]_3$

$$B\left[CH_2CH_2CH{-}CH_2CH_2CH_2B(CH_3)_2\right]_3$$
$$\qquad\quad C_6H_{11}$$

$$B\begin{matrix}[CH_2CH_2B(CH_3)_2]_2\\ CH_2CH_2CH_2B(C_2H_5)_2\end{matrix} \qquad B\begin{matrix}CH_2CH_2CH_2Al(C_2H_5)_2\\ [CH_2CH_2B(CH_3)_2]_2\end{matrix}$$

As indicated above, the compounds of this invention are particularly useful as high-energy fuels. The liquid products of this invention can be used as such in rocket and missile systems as presently designed for use of liquid fuels. The solid products of this invention can be dissolved in the simpler liquid compounds of this invention so as to give liquid compositions suitable for use in liquid fuel systems, and thereby do not suffer a decrease in energy content by virtue of the solvent used. These compounds can be used, also, for various other purposes, such as additives to improve the characteristics of conventional motor fuels, such as gasoline, jet engine fuels, etc. The methods of using these materials for such purposes employ the conventional methods now used.

While certain features of this invention have been described in detail with respect to various embodiments thereof, it will, of course, be apparent that other modifications may be made within the spirit and scope of this invention and it is not intended to limit the invention to the exact details shown above except insofar as they are defined in the following claims:

The invention claimed is:

1. A chemical compound having the formula

$$M[CR_2—(CR_2)_m—MR'_2]_3$$

wherein M is a metal selected from the class consisting of boron and aluminum, R is a radical selected from the class consisting of hydrogen, monovalent hydrocarbon groups having no more than 8 carbon atoms, and monovalent hydrocarbon groups having no more than 8 carbon atoms and having substituted thereon at least one MR'_2 group, the number of MR'_2 groups in said compound totaling no more than 10, R' is a monovalent hydrocarbon group of no more than 8 carbon atoms, and *m* is an integer having a value of at least 1 and no more than 8.

2. Tris-(beta-dimethylboro-ethyl)-borane.
3. Tris-3-dimethylboro-propyl)-borane.
4. Tris-(3-dimethylalumino-propyl)-borane.
5. Tris-(beta-dimethylalumino-ethyl)-borane.
6. Tris-(beta-dibutylboro-ethyl)-borane.
7. Tris-(3-dimethylboro-propyl)-aluane.
8. Tris-(3-dimethylalumino-propyl)-aluane.
9. Tris-(4-dimethylboro-n-butyl)-borane.
10. Tris-[bis-(dimethylboro)-butyl]-borane.
11. Tris-(beta-diethylboro-ethyl)-borane.
12. Tris-(beta-diethylboro-ethyl)-aluane.
13. A process for the preparation of a compound consisting of hydrocarbon groups and at least four metal atoms selected from the group consisting of boron and aluminum, comprising the step of reacting a combination of reagents selected from the class consisting of (1) a metal hydride having the formula MH_3 with an unsaturated metal-hydrocarbon compound having the formula $CR_2=CR(CR_2)_{m-1}MR'_2$, and (2) a disubstituted metal hydride compound having the formula R'_2MH with an unsaturated metal-hydrocarbon compound having the formula $[CR_2=CR(CR_2)_{m-1}]_3M$, in which formulas M is a metal selected from the class consisting of boron and aluminum, R represents a radical selected from the class consisting of hydrogen, monovalent hydrocarbon groups having no more than 8 carbon atoms, and monovalent hydrocarbon groups having no more than 8 carbon atoms and having substituted thereon at least one MR'_2 group, the number of MR'_2 groups in said compound totaling no more than 10, R' is a monovalent hydrocarbon group of no more than 8 carbon atoms, *m* is an integer having a value of at least 1 and no more than 8, at a temperature which effects such reaction without substantial displacement of said R' groups.

14. A process of claim 13, in which said reaction is catalyzed by a compound having at least one C—O—C structure therein and the remainder of said compound consisting of radicals selected from the group consisting of hydrocarbon groups and no more than one atom selected from the class consisting of boron and aluminum atoms.

15. A process of claim 13, in which said reaction is catalyzed by a compound having a formula selected from the group consisting of $B(OR'')_3$ and $Al(OR'')_3$ in which at least one R'' is a monovalent hydrocarbon group and the remaining R'' groups are selected from the class consisting of hydrogen and monovalent hydrocarbon groups.

16. A process of claim 13 in which said reaction is the reaction of a metal hydride having the formula MH_3 with an unsaturated metal hydrocarbon compound having the formula $CR_2=CR(CR_2)_{m-1}MR'_2$.

17. A process of claim 13 in which said reaction is the reaction of a disubstituted metal hydride compound having the formula R'_2MH with an unsaturated metal-hydrocarbon compound having the formula

$$[CR_2=CR(CR_2)_{m-1}]_3M$$

18. A process for the preparation of a compound consisting of hydrocarbon groups and boron atoms comprising the reaction of vinyl dimethyl borane with diborane, at a temperature which effects such reaction without substantial displacement of said methyl groups.

19. A process for the preparation of a compound consisting of hydrocarbon groups and aluminum and boron atoms comprising the step of reacting aluminum hydride with vinyl dimethyl borane, at a temperature which effects such reaction without substantial displacement of said methyl groups.

20. A process for the preparation of a compound consisting of hydrocarbon groups and boron comprising the step of reacting tetramethyl diborane with trivinyl borane, at a temperature which effects such reaction without substantial displacement of said methyl groups.

21. A process for the preparation of a compound consisting of hydrocarbon groups and aluminum and boron atoms, comprising the step of reacting tetramethyl diborane with trivinyl aluane, at a temperature which effects such reaction without substantial displacement of said methyl groups.

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