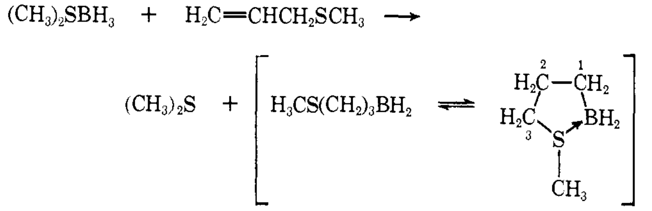
methylaminopropylborane)[5] but the product is too strongly coordinated for convenient hydroboration.

Brown also reported the hydroboration of allyl methyl sulfide with borane in diglyme in a 3:1 ratio followed by protonolysis with propionic acid to yield methyl *n*-propyl sulfide,[2b] but did not isolate any immediate hydroboration product.

We have prepared 3-(methylthio)propylborane (I) by the reaction of dimethyl sulfide–borane[6] with a small excess of allyl methyl sulfide dissolved in benzene.



I

The stability and distillable character of I are doubtless due to coordinate bonding of the sulfur to boron. However, the hydridic hydrogens are sufficiently reactive for hydroboration of carbon–carbon and carbon–nitrogen multiple bonds and reaction with alcohols.

A yield of 27 g (71% theory) was obtained from the reaction of 39 ml (0.374 mol) of dimethyl sulfide–borane added dropwise to 50 ml (0.489 mol) of allyl methyl sulfide in 100 ml of benzene, keeping the temperature below 30°. After stirring overnight, the benzene and excess reactants were distilled off (1 atm), and the product was isolated by distillation through a Vigreaux column at 44° and 1 Torr. *Anal.* Calcd for BC_4H_7S: B, 10.78; C, 47.06; H, 10.78; hydridic H, 1.96; S, 31.37. Found: B, 10.9; C, 46.8; H, 10.82; hydridic H, 1.99; S, 31.07; mol wt (freezing point depression in benzene), 98; FW, 102; density, 0.932 g/ml; refractive index, 1.5005 at 25° (leading to an atomic refractivity of 2.4 for quaternary boron, in good agreement with the value obtained with a similar nitrogen compound).[5] The infrared spectrum had a BH stretching band at 2380 cm^{-1} with a shoulder at 2360 cm^{-1}, indicating the presence of a BH_2 group. Absence of absorption in the 1500–2100-cm^{-1} region indicated absence of bridging hydrogen.[2c] The ^1H nmr spectrum of the neat liquid showed a high-field triplet at δ 0.78 which we attributed to the C-1 methylene protons, a singlet at δ 2.07 superimposed on a pentet at δ 1.90 attributed to the methyl and C-2 methylene protons, respectively, and a triplet at δ 2.33 attributed to the C-3 methylene protons. Integration of the areas corresponded to this assignment; J_{HH} = 6 Hz. Quadrupole relaxation of the boron atom minimizes the signal from hydrogen on boron and prevents appreciable coupling to the C-1 methylene protons.

When I was left in the atmosphere, a white solid was slowly formed, presumably dihydroxy(3-methylthiopropyl)borane. This melted at 48–50°. Its infrared spectrum showed no BH. Its nmr spectrum in acetone was similar to that of I, with a high-field triplet at δ 0.62, a mid-field quintet at δ 1.50, a singlet at δ 1.88, and a triplet at δ 2.67.

$$RBH_2 + 2HOH \longrightarrow RB(OH)_2 + 2H_2$$

The utility of I as an alkyl hydroborating agent was investigated on a millimolar scale by a procedure parallel to that of Brown and Subba Rao.[7] A solution of I (2.0 mmol) in 10 ml of benzene was allowed to react with the organic compound for 30 min. The reaction was then quenched with 1 ml of methanol. In a blank run, 4.0 mmol of hydrogen was evolved.

$$RBH_2 + 2CH_3OH \longrightarrow RB(OCH_3)_2 + 2H_2$$

After use of 4 mmol of cyclohexene as the organic substrate, 2 mmol of hydrogen was evolved upon addition of methanol, indicating steric hindrance to reaction of the second equivalent of cyclohexene. With borane, only 2 equiv of cyclohexene react.[2c]

After reaction with 2.0 mmol of butenenitrile, no hydrogen was evolved upon addition of methanol. Evidently both the C=C and C≡N bonds consumed hydridic hydrogen.

During reaction with 2.0 mmol of 3-butyn-1-ol, 1.84 mmol of hydrogen was evolved. None was evolved during the addition of methanol, indicating that both the hydroxyl and C≡C groups had reacted with the borane.

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Direct Observation of the Addition Products of the Reaction of Borane with Diborane and of the Reaction of Borane with Pentaborane(9)[1]

Sir:

The unstable species borane, BH_3, has long been postulated as an active intermediate in the reactions of boron hydrides; consequently, its reactions are of great interest. We have recently developed a fast-flow system with mass spectrometric analysis that has allowed the preparation of kinetically useful quantities of BH_3, and thus have been able to directly observe the reactions of BH_3.[2] This system has been used to study the self-association of borane to form diborane,[3] the reaction of borane with electron-pair

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[1] Supported by the National Science Foundation under Grant No. GP 10199.

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[3] G. W. Mappes, S. A. Fridmann, and T. P. Fehlner, *J. Phys. Chem.*, **74**, 3307 (1970).

donors,[4] and the reaction of borane with ethylene.[5] In a continuance of our objectives of identifying the facile reactions of borane and of measuring their rates, we now wish to report the existence of two reactions of borane with stable boron hydrides. In a sense, these reactions might be considered analogous to the insertion of methylene in hydrocarbons.

The flow system and the associated mass spectrometric analysis system utilizing modulated molecular beam sampling have been described elsewhere.[2,3] The use of this system for the preparation of BH_3 and the measurement of its reaction rates has also been described.[2,3] Since this work was published, a movable probe has been added to the reactor so that a reactant gas may be added at any chosen position in the reactor. The addition of a modulated counting system has improved the precision of measurement of low-level signals.[4] The experiments reported below were carried out under the following approximate conditions: BH_3 source gas, PF_3BH_3; decomposition temperature in the BH_3 preparation zone, 625°K; decomposition time, 0.4 msec; reaction temperature, 450°K; reaction time, variable from 0.3 msec; BH_3 partial pressure, 10 mTorr; B_2H_6 or B_5H_9 partial pressures, 70 mTorr; helium partial pressure, 4.7 Torr. In these experiments the stable reactant (B_2H_6 or B_5H_9) was introduced immediately downstream of the decomposition zone. Ions corresponding to products were then sought. The neutral species producing the observed ions were identified by the observed *m/e* values, the relative ion intensities, the variation of the ion signals with variation in the BH_3 and stable reactant partial pressures, the variation in the product ion intensity with time, and the relative phase of the product-ion signals.[6]

In the reaction of BH_3 with B_2H_6 the major-product ion signals were observed for *m/e* 34–40 and are given in Table I along with the uncertainties calculated on the basis of the counting statistics. The envelope of the intensities corresponds to that expected for a boron hydride.[7] The ion intensities depended on the presence of both BH_3 and B_2H_6 and decreased with decreasing reaction time. Much smaller ion peaks were observed in this region with only the BH_3 source gas on or only the B_2H_6 on. These could be due to impurities. However, B_2H_6 is the major impurity produced in the preparation of BH_3,[2] and we later showed that B_2H_6 is somewhat decomposed into BH_3 in passage through the introduction probe. It is likely, then, that these ion intensities are also due to the reaction of BH_3 with B_2H_6. By comparison with two standards (*m/e* 27 from B_2H_6 and *m/e* 58 from C_4H_{10}) the relative phase of the *m/e* 38 ion signal indicated an effective molecular weight of 38 ± 10 for the neutral progenitor of this ion. Ions were sought corresponding to tetraborane and pentaborane. Very small intensities were observed, but these cannot account for the intensities observed in the region *m/e* 34–40. The product of the reaction of BH_3 and B_2H_6 is therefore identified as a triborane. The estimated partial pressure of this species under our reaction conditions is 0.3 mTorr.

Table I. Partial Mass Spectrum of the Product of the Reaction of BH_3 with B_2H_6

m/e	Relative intensity	Uncertainty
40	9	70
39	2	20
38	100	20
37	81	20
36	62	30
35	63	40
34	51	30

In the reaction of BH_3 with B_5H_9, the major product ion signals were observed for *m/e* 67–77 and are presented in Table II along with the spectra of B_6H_{12}[8] and B_6H_{10}.[9] The envelope of intensities corresponds to that expected for a hexaborane, but the data are not good enough to say whether it is B_6H_{12} or B_6H_{10}. The ion intensities depended on the partial pressures of both BH_3 and B_5H_9. The B_5H_9 used contained an impurity having ion masses in this region with intensities *ca.* 25% of those depending on both BH_3 and B_5H_9. The latter intensities decreased with decreasing reaction time. By comparison with *m/e* 58 from C_4H_{10} and *m/e* 69 from PF_3, an effective molecular weight of the neutral progenitor of *m/e* 71 of 70 ± 10 was calculated from the relative phase of the ion signals. It seems clear that this product is a hexaborane. We estimate the partial pressure of this species under our reaction conditions as 10^{-2} mTorr.

Table II. Partial Mass Spectrum of the Product of the Reaction of BH_3 with B_5H_9

m/e	Relative intensity	Uncertainty	B_6H_{12}[c]	B_6H_{10}[d]
78			3	
77	69[b]	50	14	
76	67[b]	40	42	23
75	60[b]	30	51	34
74	71	20	72	48
73	82	20	76	49
72	100	20	100	87
71	85	20	99	100
70	78	20	68	79
69	*a*		41	58
68	70	60	29	44
67	93[b]	60	26	41

[a] Obscured by PF_3. [b] Uncorrected for B_5H_9 impurity. [c] See ref 8. [d] See ref 9.

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As we cannot observe reactions of BH_3 with rate constants less than 10^6 l./(mol sec), it is evident that BH_3 reacts quite readily with stable boron hydrides. Not only do these observations define a characteristic reaction of BH_3, but they also imply that the higher homologs of BH_3, *i.e.*, B_4H_8[10] and B_9H_{13},[11] should act in like manner. Whether they do so or not remains to be shown by experiment. The full details of these experiments will be published in due course.

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Homogeneous Catalysis of Friedel–Crafts-Type Reactions by Arene–Group VIB Tricarbonyls

Sir:

We wish to report some preliminary results of a new method of homogeneous catalysis of Friedel–Crafts-type reactions by the half-sandwich compounds $ArM(CO)_3$ (Ar = arene; M = Cr, Mo, W). We have observed that these catalysts promote reactions such as alkylation, acylation, sulfonylation, dehydrohalogenation, and polymerization, generally very conveniently and in high yields. The discussion in this paper will be confined to the Mo system, since it has been studied most extensively; however, the same reactions are promoted more or less conveniently by the Cr and W systems, research on which is currently in progress.

Table I reports some examples of the reactions investigated. Whereas the reactions appear to be general, the examples in the table are those in which products are formed in highest yields in direct reaction.

Table I. Examples of Reactions Catalyzed by $ArMo(CO)_3$

Substrate	Organic chloride	Added catalyst	[Catalyst], *M*	Reaction conditions	Comments
Toluene	*tert*-Butyl chloride	$Mo(CO)_6$	6.5×10^{-3}	Reflux, 5 hr	84.6% alkylation
Toluene	*tert*-Butyl chloride	$(tol)Mo(CO)_3$	6.5×10^{-3}	Reflux, 1 hr	81.8% alkylation
Toluene	*tert*-Butyl chloride	$AlCl_3$	Heterogeneous	Reflux, 0.75 hr	88% alkylation
Toluene	$C_6H_{11}Cl$	$Mo(CO)_6$	2.5×10^{-3}	Reflux, 24 hr	84.5% alkylation
Toluene	$C_6H_5CH_2Cl$	$Mo(CO)_6$	2.5×10^{-3}	Reflux, 12 hr	100% alkylation (90% methyl diphenylmethane; 10% polymer)
Anisole	*tert*-Butyl chloride	$Mo(CO)_6$	2.5×10^{-3}	135°, 24 hr	79% alkylation (100% para)
Phenol	*tert*-Butyl chloride	$Mo(CO)_6$	2.5×10^{-3}	Refluxing heptane, 18 hr	93% *p-tert*-butyl phenol, 3% 2,4-di-*tert*-butyl phenol
Anisole	CH_3COCl	$Mo(CO)_6$	5×10^{-3}	100°, 36 hr	68% acetylation (90% para, 4% ortho)
Toluene	Tosyl chloride	$Mo(CO)_6$	5×10^{-3}	Reflux, 36 hr	43% sulfonylation
Anisole	Tosyl chloride	$Mo(CO)_6$	5×10^{-3}	135°, 24 hr	22% sulfonylation
	$C_6H_5CH_2Cl$	$Mo(CO)_6$	5×10^{-3}	100°, 1 hr	100% polybenzyl
Durene	*p*-$ClCH_2C_6H_4CH_2Cl$	$Mo(CO)_6$	5×10^{-3}	120°, 3 hr	90% condensation polymer
Diphenyl ether	*m*-$ClSO_2C_6H_4SO_2Cl$	$Mo(CO)_6$	5×10^{-3}	Decalin solvent, 140°, 16 hr	Low to moderate yields of condensation polymer
	tert-Butyl chloride	$Mo(CO)_6$	3×10^{-2}	Reflux, 20 hr	No reaction, 96% $Mo(CO)_6$ recovered
	tert-Butyl chloride	$(tol)Mo(CO)_3$	5×10^{-2}	Reflus, 4 hr	Large amounts of HCl evolved, two polymeric substances obtained

The active form of the catalyst appears to be the arenetricarbonylmetal, rather than the hexacarbonyl, from experiments on *tert*-butyl chloride with $Mo(CO)_6$ and $ArMo(CO)_3$ (see Table I). Also shown in Table I, and supporting this view, is evidence that the catalyst decomposition products do not promote the reactions. If one of the reactants is aromatic, and the boiling point of the reaction mixture is sufficiently high (>80°), then the hexacarbonyl may be added and the catalyst generated in solution.

Although Bamford and coworkers have shown that $Mo(CO)_6$ reacts with organic halides *via* a free-radical mechanism,[1] we believe that reactions catalyzed by $ArMo(CO)_3$ proceed by way of carbonium ion generation. The polymerization of benzyl chloride, which yields polybenzyl in 100% yield in less than 1 hr, was used as a test of free-radical *vs.* carbonium ion mechanism. When the polymerization was carried out using high concentrations of free-radical traps such as galvinoxyl or 2,2-diphenyl-1-picrylhydrazyl, the reaction proceeded to completion unhindered. Alternately, when an attempt was made to promote polymerization by such free-radical initiators as azobis(isobutyronitrile), dibenzoyl peroxide, or cumene hydroperoxide, no reaction was observed. The actual mechanism of carbonium ion generation is not fully understood at this time; studies on this aspect are currently in progress.

In some of the reactions reported in Table I, the catalyst gradually decomposes and the reaction subsides. However, the reaction resumes upon further addition of small amounts of catalyst. In some cases, $ArMo(CO)_3$ can be isolated upon completion of the reaction; in these instances, addition of further amounts of the organic halide causes resumption of the reaction.

A comparison of the relative rates of reaction using preformed catalyst, $ArM(CO)_3$, and $Mo(CO)_6$ is shown in Table I. The observation that the reaction containing the preformed catalyst is much faster than that where $Mo(CO)_6$ is added and the catalyst generated in solution may be related to the fact that the rate of formation of $ArM(CO)_3$ is slow in the absence of ultraviolet light[2] or donor solvents such as diglyme.[3]

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