Organoboranes. 40. A Simple Preparation of Borinic Esters from Organolithium Reagents and Selected Boronic Esters

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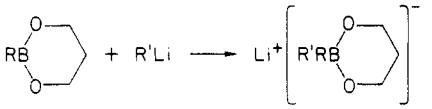
Monoorganyldiisopropoxyboranes, $RB(O\text{-}i\text{-}Pr)_2$, react cleanly at −78 °C with 1 equiv of organolithium compounds, R'Li, to form the corresponding complexes of the borinic acid esters, $LiRR'B(O\text{-}i\text{-}Pr)_2$. Treatment of these complexes with an equivalent of anhydrous hydrogen chloride in ethyl ether liberates the borinic esters, RR'BO-*i*-Pr, and isopropyl alcohol, usually readily separated by distillation. Alternatively, treatment of the complexes with 1 mol of an appropriate acid chloride liberates the borinic esters, RR'BO-*i*-Pr, and an isopropyl ester, RCO_2-*i*-Pr. By careful selection of the acid chloride, these two products can be easily separated by distillation. A careful examination of the reaction of other boronic esters in this reaction revealed that the boronic esters of 1,3-propanediol forms the 1:1 complex cleanly on reaction with organolithium compounds at −78 °C.



Treatment of these "ate" complexes either with hydrogen chloride in ether or with an appropriate acid chloride provides the pure borinic ester. Consequently, simple rational procedures are now available for the synthesis in high purities and yields of either boronic or borinic acids and esters, either through hydroboration or through the use of organolithium compounds.

The utility of boronic esters and acids as intermediates for organic synthesis[1] and as intermediates to other organoboranes[2,3] has largely been limited by the difficult availability of these compounds in pure form. A variety of methods have been used to prepare borinic esters and acids: These include the reaction of trialkylboranes with alcohols[4] and aldehydes,[5] and the thermal redistribution with boron trichloride or trialkoxyboranes. However, these methods are frequently difficult to carry out on the preparative scale.[6-8] Alternatively, the preparation of symmetrical borinic acids and esters can be obtained via hydroboration using haloboranes, BH_2Cl or BH_2Br, followed by hydrolysis or alcoholysis,[9] or by the stepwise hydridation–hydroboration of alkyldihaloboranes.[10] However, all these methods are limited to those boranes which can be readily prepared by hydroboration or simple organometallic methods, in which both or all three groups are the same. Although Mikhailov and co-workers have briefly described earlier the reaction of boronic esters with lithium reagents, their procedure was not completely general.[11-14] We describe here a simple and rational synthesis of borinic esters (or acids) by the stepwise addition of an organolithium reagent to a selected boronic ester yielding either symmetrical or unsymmetrical borinic esters. Together with the development of a rational synthesis of mixed borinic acids and esters via hydroboration, these methods make pure borinic acid intermediates readily available for further synthesis.

Table I. Methylation of Methylboronic Esters with Methyllithium

borane derivative	methylborinic ester, %	trimethylborane, %	starting material, %
methyldimethoxyborane	18	9	73
methyldiethoxyborane	22	22	56
methyldiisopropoxyborane	95	<1	<4
methyl-*tert*-butoxyborane	58	32	10
2-methyl-1,3,2-dioxaborolane	21	26	53
2-methyl-1,3,2-dioxaborinane	91	<1	<9
2-methyl-1,3,2-dioxatetramethylborolane	98	<1	<1
2-methyl-1,3,2-benzodioxaborole	20	30	50

Results and Discussion

We selected the reaction of methyllithium with various boronic esters as a test reaction. The reactions were carried out by using similar reaction conditions as reported earlier.[15,16] In most cases the boronic ester rapidly reacts with an equivalent of methyllithium in diethyl ether at −78 °C to form a mixture of complexes. These anionic complexes can be decomposed by protonation with anhydrous hydrogen chloride[11,17] at 0 °C, or by reaction with an acid

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Table II. Methylation of Organyldiisopropoxyboranes and 2-Alkyl-1,3,2-dioxaborinanes with Methyllithium

borane derivative	borinic ester, %	trialkylborane, %	starting material, %
2-methyldiisopropoxyborane	95	<1	<5
2-methyl-1,3,2-dioxaborinane	92	<7	<1
n-butyldiisopropoxyborane	86	1	13
2-*n*-butyl-1,3,2-dioxaborinane	85	4	1
tert-butyldiisopropoxyborane	87	6	7
tert-butyl-1,3,2-dioxaborinane	93	–	7
cyclohexyldiisopropoxyborane	80	6	14
2-cyclohexyl-1,3,2-dioxaborinane	87	10	3
phenyldiisopropoxyborane	94	3	3
2-phenyl-1,3,2-dioxaborinane	97	–	8

chloride, liberating a mixture of alkylmethylboranes (eq 1).

$$RB(OR')_2 + R''Li \xrightarrow[-78\ °C]{EE} Li[RR''_xB(OR')_{3-x}] \xrightarrow[\text{or } R'''COCl]{HCl,\ 0\ °C} RR''BOR' + RR''_2B + LiCl + R'OH \text{ or } R'OC(=O)R''' \quad (1)$$

The composition of these products can be estimated from the peak heights of the ^{11}B NMR spectrum for the trialkylborane and boronic and borinic esters. This method works best for compounds whose peak widths are approximately the same. The results of the reaction of various esters of methylboronic acid with methyllithium are summarized in Table I. It is apparent that there exists a wide range of selectivities toward methylation of these various esters. It is especially noteworthy that the diisopropyl, the 1,3-propanediol, and the pinacol esters of methylboronic acid give essentially one product, the dimethylalkoxyborane.

The above results can be rationalized by examining the proposed mechanism. The irreversible addition of the methyllithium to the boronic ester forms the alkylmethyldialkoxyborate 1 (eq 2). This complex, 1, is in equilibrium with the borinic ester **2** and the lithium alkoxide (eq 3). The borinic ester thus formed is susceptible to further reaction with another equivalent of methyllithium giving rise to the alkyldimethylalkoxyborate **3** (eq 4). Again this complex, **3**, is in equilibrium with the alkyldimethylborane and lithium alkoxide (eq 5). Similar steps would give rise to the formation of the tetraalkylborate species.

$$RB(OR')_2 + MeLi \rightarrow \underset{\mathbf{1}}{Li[RMeB(OR')_2]} \quad (2)$$

$$\underset{\mathbf{1}}{Li[RMeB(OR')_2]} \rightleftarrows LiOR' + \underset{\mathbf{2}}{RMeBOR'} \quad (3)$$

$$\underset{\mathbf{2}}{RMeBOR'} + MeLi \rightarrow \underset{\mathbf{3}}{Li[RMe_2BOR']} \quad (4)$$

$$\underset{\mathbf{3}}{Li[RMe_2BOR']} \rightleftarrows LiOR' + \underset{\mathbf{4}}{RMe_2B} \quad (5)$$

If the alkylmethyldialkoxyborate species 1 can be cleanly formed and the equilibrium (eq 3) favors this complex, then the borinic ester will be formed selectively on destruction of this complex. This is demonstrated in the reaction of phenyldialkoxyborane and two equivalents of methyllithium. The reaction, which was terminated by the addition of hydrogen chloride at −78 °C, gave the same selectivities as 1 equiv of methyllithium (Table II). Similarly, lithium phenylmethyldiisopropoxyborate, prepared from the borinic ester and lithium isopropoxide, and methyllithium did not produce any detectable amounts of the triorganylborane (<10%), when quenched with hydrogen chloride in ether at −78 °C. However, if this reaction was warmed to room temperature before the addition of hydrogen chloride, a complex mixture of alkylated boranes was formed. Thus the factors which affect the stability of **1** affect the selectivity of this reaction, i.e., temperature and choice of the alkoxy group, as seen in Table I. It is known that lithium methoxide is essentially insoluble in ether at room temperature, whereas lithium isopropoxide is soluble, ≥0.5 M, at −78 °C. The precipitation of relatively insoluble lithium alkoxides may shift the equilibrium (eq 2) toward the formation of the borinic ester **2** and higher alkylated boranes. While lithium *tert*-butoxide is highly soluble in ether, the reaction of methyldi-*tert*-butoxyborane gives a mixture of borane products. This presumabbly is due to the steric factors favoring dissociation of the "ate" complex. However, the above does not account for all the observed selectivities.[18]

A possible steric effect of the alkyl group of the boronic esters or the alkyllithiums is minimal for the selected esters. The reaction of various organyldiisopropoxyboranes and 2-organyl-1,3,2-dioxaborinanes with methyllithium showed little variation in the selectivity with respect to the nature of the organyl group as seen in Table II. Similar results are seen in Table III in the reaction of the various lithium reagents with these same boronic esters.

In addition to anhydrous hydrogen chloride in ether,[11,17] we also employed acetyl and benzoyl chlorides to decompose the "ate" complexes obtained by the reaction of the boronic esters with alkyllithium reagents (eq 1). In the diisopropoxyboronate ester series decomposition of the "ate" complex with hydrogen chloride/ether gives in addition to product 2-propanol (bp 82 °C), while decomposition of the "ate" complex with benzoyl chloride gives isopropyl benzoate (bp 218 °C). Thus in those cases where reaction between an alkyllithium reagents and alkyldiisopropoxyboronate produces a volatile boronic ester, i.e., dimethylisopropoxyborane (bp 52–54 °C), isolation by fractional distillation is greatly facilitated by the use of benzoyl chloride as the quenching agent. In the 1,3,2-dioxaborinane series, decomposition of the "ate" complexe with acetyl chloride leads to the volatile derivative, i.e., isopropylacetate (bp 85 °C) (760 mmHg)), and the product dimethyl(3-acetoxy-1-propoxy)borane (bp 70–72 °C (15 mmHg)), easily separated by simple distillation.

The isopropoxyborinic esters obtained by reaction of an alkyllithium reagent with a boronate ester were isolated in good yields by using the above procedures. These results are summarized in Table IV. A ^{11}B NMR analysis of the distilled isolated borinic ester indicated only trace amounts of either boronic ester or trialkylborane. Importantly, there are no observable isomerizations of the *tert*-butyl groups as analyzed by ^1H NMR, as has been reported by others.[6,15,19]

Conclusion

We have shown the unusual selectivity of some boronic esters to react cleanly with various organyllithium reagents. This was developed into a general procedure for the preparation of symmetrical and unsymmetrical borinic esters and also borinic esters containing organic groups which cannot be prepared via hydroboration. We now have available rational synthetic procedures for the syn-

(18) In some cases the other esters give clean formation of the borinic esters: i.e., *tert*-butyldimethoxyborane cleanly reacts with methyl or *tert*-butyllithium to give the desired products in 83 and 95% selectivity.

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Table III. Alkylation of Alkyldiisopropoxyboranes and 2-Alkyl-1,3,2-dioxaborinanes with Alkyllithiums

borane derivative	alkyllithium	borinic ester, %	trialkylborane, %	starting material, %
methyldiisopropoxyborane	isopropyl	86	1	13
methyldiisopropoxyborane	*tert*-butyl	92	<1	<8
methyldiisopropoxyborane	phenyl	95	2.5	2.5
2-methyl-1,3,2-dioxaborinane	*tert*-butyl	80	5	15
2-methyl-1,3,2-dioxaborinane	phenyl	92	<7	<1
n-butyldiisopropoxyborane	isopropyl	85	5	10
n-butyldiisopropoxyborane	*tert*-butyl	88	6	6
n-butyldiisopropoxyborane	phenyl	86		14
2-*n*-butyl-1,3,2-dioxaborinane	*tert*-butyl	82	4	14
2-*n*-butyl-1,3,2-dioxaborinane	phenyl	92		8
2-*n*-butyl-1,3,2-dioxaborinane	isopropyl	85	5	10
tert-butyldiisopropoxyborane	isopropyl	85	4	11
tert-butyldiisopropoxyborane	*tert*-butyl	88	5	7
tert-butyldiisopropoxyborane	phenyl	90	3	7
2-*tert*-butyl-1,3,2-dioxaborinane	*tert*-butyl	90		10
2-*tert*-butyl-1,3,2-dioxaborinane	phenyl	90		10
2-*tert*-butyl-1,3,2-dioxaborinane	isopropyl	90	4	6
cyclohexyldiisopropoxyborane	isopropyl	82	2	16
cyclohexyldiisopropoxyborane	*tert*-butyl	94		6
cyclohexyldiisopropoxyborane	phenyl	92		8
2-cyclohexyl-1,3,2-dioxaborinane	isopropyl	81	3	16
2-cyclohexyl-1,3,2-dioxaborinane	*tert*-butyl	82		18
2-cyclohexyl-1,3,2-dioxaborinane	phenyl	74	13	13
phenyldiisopropoxyborane	isopropyl	92	4	4
phenyldiisopropoxyborane	*tert*-butyl	86	5	9
phenyldiisopropoxyborane	phenyl	90		10
2-phenyl-1,3,2-dioxaborinane	isopropyl	89		11
2-phenyl-1,3,2-dioxaborinane	*tert*-butyl	88		12
2-phenyl-1,3,2-dioxaborinane	phenyl	89		11

Table IV. Yields and Properties of Isolated Borinic Esters

borinic ester	yield, %	n_D^{20}	bp, °C (mmHg)
dimethylisopropoxyborane	82	1.3572	52–54 (758)
methyl-*tert*-butylisopropoxyborane	84	1.3883	90–92 (741)
methylphenylmethoxyborane	82	1.4500	78–80 (15)
methylphenylisopropoxyborane	90	1.4838	54 (0.1)
tert-butylphenylisopropoxyborane	86	1.4617	94–96 (15)
di-*tert*-butylisopropoxyborane	86	1.4125	54 (15)
n-butyl-*tert*-butylisopropoxyborane	75	1.4044	68–70 (15)
isopropylphenylisopropoxyborane	84	1.4727	106–108 (15)
diphenylisopropoxyborane	82	1.544	88 (0.1)
cyclohexylphenylisopropoxyborane	91	1.4998	66–68 (0.1)
cyclohexylmethyl(3-acetoxy-1-propoxy)borane	65	1.4486	92–94 (0.1)
dimethyl(3-acetoxy-1-propoxy)borane	74	1.4054	70–72 (15)

thesis in high purity and yields boronic and borinic acids and esters either through hydroboration,[9,10] or the use of organolithium compounds,[15] or a combination of the two approaches. These compounds are now available for use as intermediates or conversion to other organoboranes.

Experimental Section

General Comments. All glassware was dried at 140 °C for at least 3 h, assembled hot, and cooled under a stream of nitrogen. Anhydrous ethyl ether (Mallinkrodt) was stored over 4-Å molecular sieves under nitrogen and was used without further purification.

The organolithium reagents (*n*-butyllithium, methyllithium, and phenyllithium) are commercial materials (Aldrich or Alfa); isopropyllithium was prepared according to the procedure of Gilman.[20] The concentrations were standardized prior to use. The borane esters were prepared according to standard procedures.[16,21] The anhydrous hydrogen chloride in ether solution (ca. 3 M) were prepared by using a Brown□ apparatus from hydrochloric acid and sulfuric acid.[22] The solutions were standardized by hydrolyzing an aliquot in water and titrating with a standard solution of sodium hydroxide. Acetyl chloride and benzoyl chloride were distilled from CaH_2 and stored under nitrogen.

The ^1H NMR spectra were recorded on a Varian T-60 (60-MHz) spectrometer, relative to tetramethylsilane. ^{11}B NMR were obtained on a Varian FT-80A spectrometer (25.517 MHz) relative to boron trifluoride etherate. Infrared spectra were obtained on a Perkin-Elmer1420 ratio recording infrared spectrometer. UV spectra were run on a Carey 17D instrument. Mass spectra were obtained on a Finnigan, Model 4000, gas chromatographic mass spectrometer. Microanalysis was performed in house.

General Procedure Determining the Selectivity of Alkyllithium Alkylation with Various Boronic Esters. To a 50-mL centrifuge tube fitted with a magnetic stirring bar and rubber septum was added via syringe 2–6 mmol of the boronic ester and 4–12 mL of ether to give an initial concentration of ca. 0.5 M. The solution was cooled to −78 °C with a dry ice/acetone bath, and 1 equiv of alkyllithium reagent was slowly added dropwise via a syringe. The resulting mixture was stirred at −78 °C for 3 h. Then either 1 equiv of anhydrous hydrogen chloride or acid chloride was added. The cooling bath was removed and the mixture allowed to warm to room temperature and stirred for an additional 15 min. A sample was removed for analysis by ^{11}B NMR for the various alkylated boranes. The percentage of trialkylboranes, starting material, and product borinic ester were estimated by using peak height. This procedure appears to give good mass balances, ±5%, for compounds with similar peak widths at half-height. The results are shown in Table I–III.

General Procedure for the Isolation of Borinic Esters. To a round-bottom flask fitted with a magnetic stirring bar and adaptor was added 25–100 mmol of the boronic ester in 50–200 mL of ether to give an initial concentration of ca. 0.5 M. The solution was cooled in a dry ice/acetone bath. An equivalent of alkyllithium was added dropwise via a double-ended needle in 30–45 min. The reaction was stirred for 3 h, then quenched with the addition of an equivalent of hydrogen chloride in ether or with

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neat acid chloride, and warmed to room temperature. The clear ether solution was decanted from the lithium chloride precipitate and combined with the ether washes of the solid. After the ether was removed either by atmospheric distillation or under reduced pressure, the residual material was distilled at atmospheric or reduced pressure. Only a small amount of residual material remained after distillation. The results are summarized in Table IV.

Preparation of *tert*-Butylmethylisopropoxylborane. The reaction was conducted as described above by using methyldiisopropoxyborane (5.76 g, 40 mmol) and *tert*-butyllithium (24.2 mL, 40 mmol). Distillation yielded 5.28 g (33.4 mmol, 84%): bp 90–92 °C (741 mmHg); n^{20}_D 1.3883: proton NMR ($CDCl_3$) 4.30 (septet, J = 18 Hz, 1 H), 1.15 (d, J = 18 Hz, 6 H), 0.83 (s, 9 H), 0.30 ppm (br s, 3 H); boron NMR (neat) +52.9 ppm (s); mass spectrum (chemical ionization isobutane), m/e 143 (M + 1, 100%). Anal. Calcd for $C_8H_{19}BO$: C, 67.70; H, 13.40; B, 7.62. Found: C, 67.20; H, 13.65; B, 7.21.

Methylphenylisopropoxyborane. The reaction was carried out as described above using methyldiisopropoxyborane (7.3 g, 50.7 mmol) and phenyllithium (28.2 mL, 50.7 mmol). Distillation yielded 7.4 g (54.7 mmol, 90%): bp 54 °C (0.1 mmHg); n^{20}_D 1.4838; proton NMR ($CDCl_3$) 7.83 (m, 2 H), 7.30 (m, 3 H), 4.53 (septet, J = 18 Hz, 1 H), 1.25 (d, J = 18 Hz, 6 H), 0.73 ppm (br s, 3 H); boron NMR (neat) +47.2 ppm (s); mass spectrum (chemical ionization, isobutane), m/e 163 (M + 1, 48%); MS (EI, 70 eV), m/e 162 (M, 0.3%); UV (hexane) λ_{max} (ϵ) 227 (10970). Anal. Calcd for $C_{10}H_{15}BO$: C, 74.17; H, 9.27; B, 6.67. Found: C, 74.17; H 9.60; B, 6.24.

***tert*-Butylphenylisopropoxyborane.** With *tert*-butyldiisopropoxyborane (8.38 g, 45.1 mmol) and phenyllithium (23 mL, 45.1 mmol) this reaction was conducted as described above. Distillation yielded 7.9 g (38.8 mmol, 86%): bp 94–96 °C (15 mmHg); n^{20}_D 1.4617; proton NMR ($CDCl_3$) 7.23 (br s, 5 H), 4.13 (septet, J = 18 Hz, 1 H), 1.08 (d, J = 18 Hz, 6 H), 0.90 ppm (s, 9 H); boron NMR (neat) +49.9 ppm (s). Anal. Calcd for $C_{13}H_{21}BO$: C, 76.55; H, 10.30; B, 5.30. Found: C, 76.24, H, 10.30; B, 4.96.

Di-*tert*-butylisopropoxyborane. The reaction was carried out as described above by using *tert*-butyldiisopropoxyborane (7.20 g, 38.7 mmol) and *tert*-butyllithium (23.5 mL, 38.7 mmol). Distillation of the residue yielded 4.73 g (33.1 mmol, 86%): bp 54 °C (15 mmHg); n^{20}_D 1.4125; proton NMR ($CDCl_3$) 4.77 (septet, J = 18 Hz, 1 H), 1.18 (d, J = 18 Hz, 6 H), 1.00 ppm (s, 18 H); boron NMR (neat) +49.9 ppm (s); mass spectrum (chemical ionization, isobutane), m/e 185 (M + 1, 15%). Anal. Calcd for $C_{11}H_{25}BO$: C, 71.82; H, 13.60; B, 5.88. Found: C, 71.30; H, 13.93; B, 5.39.

***n*-Butyl-*tert*-butylisopropoxyborane.** The reaction was carried out as described above by using *n*-butyldiisopropoxyborane (8.49 g, 45.6 mmol) and *tert*-butyllithium (28 mL, 46 mmol). Distillation of the residue yielded 6.29 g (34.2 mmol, 75%): bp 68–70 °C (15 mmHg); n^{20}_D 1.4044; proton NMR ($CDCl_3$) 4.37 (septet, J = 18 Hz, 1 H), 1.15 (d, J = 18 Hz, 6 H), 0.83 ppm (s, 9 H); boron NMR (neat) +52.2 ppm (s); mass spectrum (chemical ionization, isobutane), m/e 185 (M + 1, 100%). Anal. Calcd for $C_{11}H_{25}BO$: C, 71.82; H, 13.60; B, 5.88. Found: C, 71.06; H, 13.82; B, 5.44.

Isopropylphenylisopropoxyborane. The reaction was conducted as described above by using phenyldiisopropoxyborane (4.64 g, 22.5 mmol) and isopropyllithium (40 mL, 22.8 mmol). Distillation yielded 3.6 g (18.9 mmol, 84%): bp 106–108 °C (15 mmHg); n^{20}_D 1.4727; proton NMR ($CDCl_3$) 7.57 (m, 5 H), 4.47 (septet, J = 18 Hz, 1 H), 1.22 (d, J = 18 Hz, 6 H), 1.02 ppm (br d, J = 15 Hz, 6 H); boron NMR (neat) +48.6 ppm (s); mass spectrum (chemical ionization, isobutane), m/e 191 (M + 1, 7.4%); UV (hexane) λ_{max} (ϵ) 220 (17510), 235 nm (sh 8190). Anal. Calcd for $C_{12}H_{19}BO$: C, 75.87; H, 10.01; B 5.69. Found: C, 76.03; H, 10.09; B, 5.27.

Diphenylisopropoxyborane. The reaction procedure is described above by using phenyldiisopropoxyborane (9.04 g, 43.9 mmol) and phenyllithium (22 mL, 44.0 mmol). Distillation of the residue after removal of the ether yielded 8.56 g (38.3 mmol, 87%): bp 88–89 °C (0.1 mmHg); n^{20}_D 1.544; proton NMR ($CDCl_3$) 7.57 (m, 2 H), 7.37 (m, 3 H), 4.57 (septet, J = 18 Hz, 1 H), 1.25 ppm (d, J = 18 Hz, 6 H); boron NMR (neat) +44.8 ppm (s); mass spectrum (chemical ionization, isobutane), m/e 225 (M + 1, 17%); UV (hexane) λ_{max} (ϵ) 237 nm (18560). Anal. Calcd for $C_{15}H_{17}BO$: C, 80.43; H, 7.60; B, 4.83. Found: C, 80.05; H, 7.54; B, 4.66.

Cyclohexylphenylisopropoxyborane. The reaction was conducted as described above by using cyclohexyldiisopropoxyborane (5.31 g, 25.3 mmol) and phenyllithium (14.1 mL, 25.3 mmol). Distillation yielded 5.3 g (23 mmol, 91%): bp 66–68 °C (0.1 mmHg); n^{20}_D 1.4998; proton NMR ($CDCl_3$) 7.30 (m, 5 H), 4.43 (septet, J = 18 Hz, 1 H), 1.50 (m, 11 H), 1.18 ppm (d, J = 18 Hz, 6 H); boron NMR (neat) +48.7 ppm (s); mass spectrum (chemical ionization, isobutane), m/e 231 (M + 1, 7%); MS (EI, 70 eV), m/e 230 (M, 3%). Anal. Calcd for $C_{15}H_{23}BO$: C, 78.33, H, 10.00; B, 4.70. Found: C, 78.23; H, 10.35; B, 4.33.

Methylcyclohexyl(3-acetoxy-1-propoxy)borane. The reaction was carried out by using 2-cyclohexyl-1,3,2-dioxaborinane (9.27 g, 55.2 mmol) and methyllithium (35.4 mL, 55.2 mmol) using the procedure described above and quenching with acetyl chloride (4.33 g, 55.2 mmol). Distillation yielded 8.1 g (35.8 mmol, 65%): bp 92–94 °C (0.1 mmHg); n^{20}_D 1.4486; proton NMR ($CDCl_3$) 4.00 (q, J = 18 Hz, 4 H), 2.03 (s, 3 H), 0.30 ppm (s, 3 H); boron NMR (neat) +53.3 ppm (s); mass spectrum (chemical ionization, isobutane), m/e 227 (M + 1, 100%); IR (thin film) 1742 cm^{-1}. Anal. Calcd for $C_{12}H_{23}BO_3$: C, 63.77, H, 10.19; B, 4.78. Found: C, 63.61; H, 10.46; B, 4.56.

Dimethyl(3-acetoxy-1-propoxy)borane. The reaction was carried out by using 2-methyl-1,3,2-dioxaborinane (5.0 g, 50 mmol) and methyllithium (31.3 mL, 50 mmol) using the procedure described above and quenching with acetyl chloride (3.93 g, 50 mmol). Distillation yielded 5.9 g (33 mmol, 74%): bp 70–72 °C (15 mmHg); n^{20}_D 1.4054; proton NMR ($CDCl_3$) 4.07 (m, 4 H), 2.03 (s, 3 H), 1.95 (m, 2 H), 0.37 ppm (s, 3 H); boron NMR (neat) +53.3 ppm (s); mass spectrum (chemical ionization, isobutane), m/e 159 (M + 1, 16%); IR (thin film) 1742 cm^{-1}. Anal. Calcd for $C_7H_{15}BO_3$: C, 53.22; H, 9.57; B, 6.84. Found: C, 53.45; H, 9.65; B, 6.59.

Methylphenylmethoxyborane. The reaction using 2-methyl-1,3,2-dioxaborinane (2.02 g, 20.6 mmol) and phenyllithium (11.4 mL, 20.6 mmol) was carried out as described above and then quenched with excess dilute hydrochloric acid (1:1). The reaction was allowed to warm to room temperature and stirred for an additional 15 min. The aqueous phase was removed via double-ended needle and the ether removed at reduced pressure. The borinic ester was esterified in pentane (20 mL) with methanol (1.32 g, 41.2 mmol), 0.5 h. The pentane solution was dried with magnesium sulfate and transferred to a distillation flask, along with a 20-mL wash of the solid. Distillation yielded 2.2 g (16.4 mmol, 82%): bp 78–80 °C (15 mmHg); n^{20}_D 1.4500; proton NMR ($CDCl_3$) 7.87 (m, 2 H), 7.30 (m, 3 H), 3.53 (s, 3 H), 0.53 ppm (br s, 3 H); boron NMR (neat) +48.1 ppm (s); mass spectrum (chemical ionization, isobutane), m/e 135 (M + 1, 100%); MS (EI, 70 eV), m/e 134 (M, 29%); UV (hexane) λ_{max} (ϵ) 227 nm (11765). Anal. Calcd for $C_8H_{11}BO$: C, 71.75; H, 8.22; B, 8.07. Found: C, 71.72; H, 8.25; B, 7.88.

Dimethylisopropoxyborane. Diisopropoxymethylborane (15.3 g, 106 mmol) and methyllithium (66.3 mL, 106 mmol) were reacted as described above. The reaction was quenched with benzoyl chloride (14.9 g, 106 mmol). After the usual workup, fractional distillation on a Todd column, 30 cm, yielded 8.7 g (87 mmol, 82%): bp 52–54 °C (758 mmHg); n^{20}_D 1.3572; proton NMR ($CDCl_3$) 4.40 (septet, J = 18 Hz, 1 H), 1.19 (d, J = 18 Hz, 6 H), 0.37 ppm (br s, 6 H); boron NMR (neat) +52.1 ppm (s). Anal. Calcd for $C_5H_{13}BO$: C, 60.12; H, 13.03; B, 10.82. Found: C, 59.68; H, 17.71; B, 10.37.

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Registry No. **2** (R = R′ = Me), 4443-43-0; **2** (R = Me, R′ = Et), 86610-16-4; **2** (R = Me, R′ = *i*-Pr), 95407-90-2; **2** (R = Me, R′ = *t*-Bu), 38109-66-9; **2** (R = Me, R′ = $(CH_2)_2OH$), 97782-66-6; **2** (R = Me, R′ = $(CH_2)_3OAc$), 97782-67-7; **2** (R = Me, R′ = $C(CH_3)_2C(CH_3)_2OH$), 97782-68-8; **2** (R = Me, R′ = *o*-C_6H_4OH), 97782-69-9; **2** (R = *n*-Bu, R′ = *i*-Pr), 97782-71-3; **2** (R = *n*-Bu, R′ = $(CH_2)_3OH$), 97782-72-4; **2** (R = *t*-Bu, R′ = *i*-Pr), 97782-73-5; **2** (R = *t*-Bu, R′ = $(CH_2)_3OH$), 97782-74-6; **2** (R = cyclohexyl, R′

= *i*-Pr), 97782-75-7; **2** (R = cyclohexyl, R′ = $(CH_2)_3OAc$), 97782-76-8; **2** (R = Ph, R′ = *i*-Pr), 97782-77-9; **2** (R = Ph, R′ = $(CH_2)_3OH$), 97782-78-0; **2** (R = R′ = *i*-Pr), 97782-79-1; **2** (R = *t*-Bu, R′ = $(CH_2)_3OH$), 97782-74-6; **2** (R = Ph, R′ = $(CH_2)_3OH$), 97782-80-4; $MeB(OMe)_2$, 7318-81-2; $MeB(OEt)_2$, 86595-26-8; $MeB(OPr\text{-}i)_2$, 86595-27-9; $MeB(OBu\text{-}t)_2$, 819-38-5; MeLi, 917-54-4; *n*-$BuB(OPr\text{-}i)_2$, 86595-32-6; *t*-$BuB(OPr\text{-}i)_2$, 86595-34-8; $PhB(OPr\text{-}i)_2$, 1692-26-8; *i*-PrLi, 1888-75-1; *t*-BuLi, 594-19-4; PhLi, 591-51-5; 2-methyl-1,3,2-dioxaborolane, 37003-57-9; 2-methyl-1,3,2-dioxaborinane, 51901-48-5; 2-methyl-1,3,2-dioxatetramethylborolane, 94242-85-0; 2-methyl-1,3,2-benzodioxaborole, 51901-49-6; 2-*n*-butyl-1,3,2-dioxaborinane, 30169-71-2; *tert*-butyl-1,3,2-dioxaborinane, 63689-73-6; cyclohexyldiisopropoxyborane, 97782-70-2; 2-cyclohexyl-1,3,2-dioxaborinane, 30169-75-6; 2-phenyl-1,3,2-dioxaborinane, 4406-77-3; *n*-butylisopropylisopropyborane, 97782-81-5; *n*-butyl-*tert*-butylisopropoxyborane, 97782-82-6; *n*-butylphenylisopropoxyborane, 97782-83-7; *n*-butyl-*tert*-butyl(3-hydroxypropoxy)borane, 97782-84-8; *n*-butylphenyl(3-hydroxypropoxy)borane, 97782-85-9; *n*-butylisopropyl(3-hydroxypropoxy)borane, 97782-86-0; *tert*-butylisopropylisopropoxyborane, 97782-87-1; di-*tert*-butylisopropoxyborane, 86595-35-9; *tert*-butylphenylisopropoxyborane, 97782-88-2; di-*tert*-butyl(3-hydroxypropoxy)borane, 97782-89-3; *tert*-butylphenyl(3-hydroxypropoxy)borane, 97782-90-6; *tert*-butylisopropyl(3-hydroxypropoxy)borane, 97782-91-7; cyclohexylisopropylisopropoxyborane, 97782-92-8; *tert*-butylcyclohexylisopropoxyborane, 97782-93-9; phenylcyclohexylisopropoxyborane, 97782-94-0; *tert*-butylcyclohexyl(3-hydroxypropoxy)borane, 97782-95-1; isopropylcyclohexyl(3-hydroxypropoxy)borane, 97782-99-5; phenylcyclohexyl(3-hydroxypropoxy)borane, 97782-96-2; phenylisopropylisopropoxyborane, 97782-97-3; diphenylisopropoxyborane, 69737-51-5; isopropylphenyl(3-hydroxypropoxy)borane, 97782-98-4; diphenyl(3-hydroxypropoxy)borane, 74666-84-5; acetyl chloride, 75-36-5; benzoyl chloride, 98-88-4.

$(\mu\text{-}H)_2M_3(CO)_8(\mu\text{-}PPh_2)_2$ (M = Fe, Ru, Os): An Isostructural Triad of Phosphido-Bridged Hydrides. Rational Synthesis and Structural Characterization

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The synthesis and structural characterization of the triad of phosphido-bridged hydrido clusters $(\mu\text{-}H)_2M_3(CO)_8(\mu\text{-}PPh_2)_2$ (**1**, M = Fe, **2**, M = Ru, and **3**, M = Os) are described. The triiron cluster **1** has been prepared via the reaction of Ph_2PH with the protonated anion $Fe_4(CO)_{13}^{2-}$. The ruthenium and osmium congeners have been obtained from the phosphine complexes $M_3(CO)_{10}(PPh_2H)_2$ via oxidative addition of the P–H bonds of the secondary phosphines to the clusters. Crystals of **1**–**3** are triclinic of space group $P\bar{1}$ with unit cell dimensions. **1**: a = 10.918 (2) Å, b = 11.898 (2) Å, c = 14.705 (2) Å; α = 75.02 (1)°, β = 84.72 (1)°, γ = 70.84 (1)°. **2**: a = 11.150 (1) Å, b = 12.027 (1) Å, c = 14.693 (1) Å; α = 76.03 (1)°, β = 84.70 (1)°, γ = 70.24 (1)°. **3**: a = 11.184 (1) Å, b = 11.991 (1) Å, c = 14.657 (1) Å; α = 76.17 (1)°, β = 84.72 (1)°, γ = 70.01 (1)°. The structures were solved and refined to the following R and R_w values; **1**, R = 0.034, R_w = 0.039 on 4243 observed ($I \geq 3\sigma(I)$) data; **2**, R = 0.023, R_w = 0.027 on 5478 data; **3**, R = 0.038, R_w = 0.048 on 5325 data. The three molecules are isostructural with a triangular framework of metal atoms supported on two adjacent sides by phosphido and hydrido bridges, one metal–metal vector being unbridged. The change in structural parameters down the triad and reactions with carbon monoxide are discussed.

Introduction

The search for strongly bound yet flexible bridging ligands capable of maintaining two or more metal fragments in close proximity both within and beyond the regimes of metal–metal bonding has stimulated interest in the chemistry of phosphido-bridged systems.[1] Although there is now abundant evidence that phosphido bridges may be noninnocent ligands[1,2] and hence cannot be discounted as sites of reactivity, there are also substantial indications of potentially useful chemical transformations on PR_2-bridged bi- and polynuclear compounds.[1,3]

One class of phosphido-bridged compounds which has not yet attracted much attention is the group of μ-hydrido,

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