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Recent Advances in Phosphinoborane Chemistry[†]

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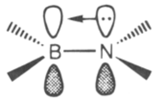
Contents

I. Introduction

Until recently, textbooks taught that σ and π bonding between third row and heavier main-group elements was inherently weak and would preclude the formation of alkane-like, olefin-like, and arene-like homologues of well-known organic compounds. Consequently, until the late 1980s, little effort was given to developing appropriate synthetic approaches to these compounds, and chemical and structural parallels between main-group and organic compounds beyond short-chain alkane and carbene analogues were few.

On a seemingly unrelated front, rapid developments in organotransition metal chemistry during the 1970s revealed that some unstable coordinatively unsaturated and/or electron-deficient metal fragments could be stabilized by bulky substituents on or near reactive centers. By adopting these steric congestion/protection principles, disilenes, the first examples of compounds containing heavy main-group element multiple bonds, were subsequently isolated.[1,2] Dramatic new findings continue to appear in this area, and a fascinating array of multiply bonded and catenated compounds of Si, Ge, Sn, P, and As are now known, and many of these compounds display striking parallels with organic compounds.

Isoelectronic principles suggest that there should exist extensive parallels between organic carbon compounds and compounds containing boron and nitrogen.[3] Indeed, the very existence of some classes of organic compounds has stimulated attempts to prepare analogous B−N compounds. To some degree, these efforts have been successful. Some isoelectronic/isolobal connections that have been established include alkanes $R_3CCR_3 \underset{\circ}{\leftrightarrow}$ amine boranes R_3NBR_3, cyclobutane $\underset{\circ}{\leftrightarrow}$ dimeric aminoboranes $(R_2BNR_2)_2$, alkenes $R_2CCR_2 \underset{\circ}{\leftrightarrow}$ aminoboranes R_2NBR_2, cyclobutenes $(RCCR)_2 \underset{\circ}{\leftrightarrow}$ diazadiboretidines $(RNBR)_2$, benzene $(RCCR)_3 \underset{\circ}{\leftrightarrow}$ borazine $(RNBR)_3$, and alkynes $RCCR \underset{\circ}{\leftrightarrow}$ iminoboranes RNBR.[3] Although the structural parallels in most cases are strong, it is also apparent that boron−nitrogen bonds are more electronically asymmetric than C−C bonds. The boron atom electron deficiency and σ bond polarity are partially offset by nitrogen lone pair donation to the empty boron p_z orbital, as represented in **1**, but the



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[†] The following abbreviations are used in the text: X = general substituent; R = organic substituent; Hal = halogen; Me = CH_3; Et = C_2H_5; ^{i}Pr = $CH(CH_3)_2$; Bu = $(CH_2)_3CH_3$; ^{t}Bu = $C(CH_3)_3$; ^{i}Bu = $CH_2CH(CH_3)_2$; BBN = 9-borabicyclo[3.3.1]nonyl; 1-Ad = 1-adamantyl; Ph = C_6H_5; Mes = 2,4,6-$(CH_3)_3C_6H_2$; Ar* = 2,4,6-$[C(CH_3)_3]_3C_6H_2$; Thex = $(CH_3)_2CH[(CH_3)_2C]$; Cy = C_6H_{11}; Trip = 2,4,6-$[(CH_3)_2CH]_3C_6H_2$; Tmp = 2,2,6,6-tetramethylpiperidino; DME = ethylene glycol dimethyl ether; THF = tetrahydrofuran.

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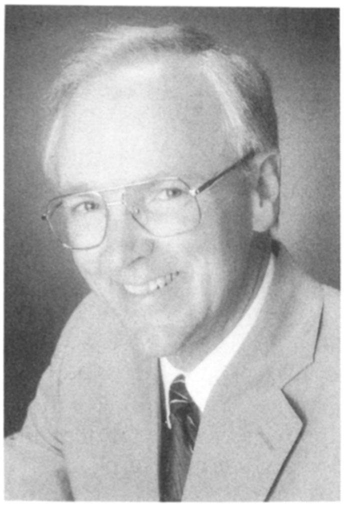


Robert T. Paine was born in Colorado Springs, CO, in 1944. He received his B.S. degree from the University of California, Berkeley (1966), and his Ph.D. (with R. W. Parry) from the University of Michigan (1970). Following postdoctoral studies at Northwestern University and Los Alamos National Laboratory, he joined the faculty at the University of New Mexico as an Assistant Professor in 1974. In 1983 he was appointed Professor of Chemistry. His current research interests are in the development of main-group, polymeric precursors to solid-state materials, the design of metal ion-specific organic extractants, and immobilization of these extractants on solid supports and membranes, and the formation of new main-group ring and cluster configurations.

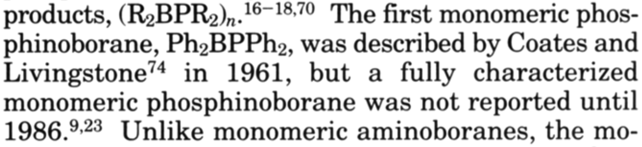
Professor Dr. H. Nöth was born in 1929. He received his Ph.D. under the supervision of Professor E. Wiberg at the University of Munich. Professor Nöth was appointed Professor of Inorganic Chemistry at the University of Marburg in 1966. In 1969 he moved to the University of Munich where he is now Director of the Institute of Inorganic Chemistry. He was president of the German Chemical Society for the periods 1988/89 and 1992/93. Dr. Nöth is the author of more than 500 publications. His current research interests involve the chemistry of hydrogen compounds, nitrogen-bonded compounds of boron, phosphorus, and arsenic (particularly highly reactive species, cations, heterocycles, and cage compounds), coordination compounds with metal–boron bonding, heterocyclic π-complexes, NMR spectroscopy, and X-ray structure determinations. In his spare time, he plays the piano and practices mountain biking and gardening.

extent of π delocalization in potentially conjugated molecules is significantly reduced. This is verified by reaction chemistry of the boron−nitrogen compounds that differs in dramatic ways from carbon chemistry.[4-6] Nonetheless, advances in heavy group 14 element chemistry,[1,2] as well as successful searches[4,7,8] for the first monomeric aminoiminoboranes, $R_2NB{=}NR$, and organoimino boranes, $RB{=}NR$, guided by isoelectronic reasoning have encouraged new efforts to establish structurally related heavy atom congeners of carbon and boron−nitrogen compounds. In particular, Power[9-22] Cowley,[23,24] Fritz,[25-27] Baudler,[28-31] Escudié,[32,33] Karsch,[34,35] Paetzold,[36,37] Siebert,[38-41] Nöth,[42-51] and our combined groups[52-69] have been active in developing C/BN parallels in boron−phosphorus chemistry. Aspects of this topic were initially reviewed by Sowerby,[70] and more recent accounts have been provided by Power.[18-20] The area is healthy and it continues to expand in many exciting directions. We recount in this review selected pertinent aspects of the early work; however, primary focus is given to developments since 1985.

II. Monomeric Phosphinoboranes

The simplest hydrocarbon/boron−nitrogen/boron−phosphorus compound analogy involves alkanes ↔ amine boranes ↔ phosphane boranes. Hundreds of phosphane borane complexes, $X_3B{:}PY_3$, are known;[71] however, these compounds will not be discussed here. Instead, coverage begins with monomeric phosphinoboranes, R_2BPR_2, that may be compared with monomeric aminoboranes and alkenes.

The classical carbon−carbon double bond is characterized by the combination of C sp^2-C sp^2 σ overlap and C−C π overlap that results in a planar C atom geometry, short C−C bond distance, 1.34 Å (avg), and a high barrier to C−C bond rotation. These bonding interactions also give rise to electronic and coordinative saturation at the C atoms, and there is no *natural* tendency for alkenes to undergo head-to-tail association that would produce dimeric (cyclobutane) or trimeric (cyclohexane) species. As alluded to above, monomeric aminoboranes, R_2BNR_2, also display an ethylene-like planar ground state with three-coordinate B and N atoms, short B−N bond distance, 1.38 Å (avg), and relatively high barrier to B−N bond rotation.[72] However, in contrast to an alkene, the formal B−N double bond is polar, and the N atom retains a good deal of its lone pair character. Without steric shielding of the B and/or N atoms or proper electronic assistance, these coordinatively unsaturated fragments undergo head-to-tail oligomerization and produce four- or six-membered ring analogues of cyclobutane and cyclohexane as well as oligomers.[73]



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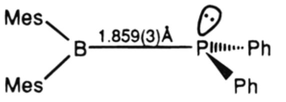
On the other hand, with steric protection, "ethylenic" aminoborane monomers are isolated.

Similarly, all early attempts to prepare monomeric phosphinoboranes gave head-to-tail condensation products, $(R_2BPR_2)_n$.[16-18,70] The first monomeric phosphinoborane, Ph_2BPPh_2, was described by Coates and Livingstone[74] in 1961, but a fully characterized monomeric phosphinoborane was not reported until 1986.[9,23] Unlike monomeric aminoboranes, the molecular structure determinations for Mes_2BPPh_2[9] (**2**) and TmpB(Cl)P(H)Mes[23] (**3**) revealed that the phosphorus atom in these phosphinoborane monomers is pyramidal. The P−B bond distance in **3** is long and typical of a P−B single bond while the B−P distance in **2** is intermediate between a B−P single-bond distance (1.90–2.00 Å) and double-bond distance (1.79–1.84 Å).[19] It was subsequently reported that, with increased steric shielding, **4** adopts a planar P atom geometry with a short B–P bond distance consistent with the presence of some degree of π overlap between the B and P atoms.[21]



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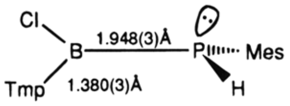

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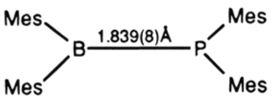

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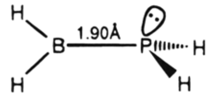
The topic of pπ–pπ orbital overlap involving boron and other main-group atoms has been heavily debated over the last 40 years, and the results from a series of theoretical analyses of $H_2B{-}X$ (X = NH_2, OH, PH_2, and SH) species[75–79] are illuminating with respect to the experimental observations outlined above. Briefly, the C_s symmetry structure **5** with a pyramidal phosphorus atom is more stable than the fully planar C_{2v} structure **6**, although the energy difference is not large (~6 kcal/mol).[77] Furthermore, Allen and co-workers[77] have analyzed orbital kinetic energies for these two structures and, as expected, found that the two electrons in the π orbital of the planar structure **6** were not evenly distributed between the B and P atoms. Instead, the electrons are enormously stabilized by transfer to a P atom lone pair-like orbital. A σ(BH) orbital is also stabilized in this process, but these shifts are largely offset by σ orbital destabilizations in the rest of the molecule. Orbital contour maps also indicate that the B–P π orbital in **6** is largely concentrated on the P atom and only weakly associated with the B atom. It is interesting to note, however, that the contour map describing the P atom lone pair-dominated HOMO in the single-bond structure **5** shows that the localized lone pair orbital is accompanied by a small component of B–P π bonding on the "underside" of the molecule, as illustrated schematically by **7**. The residual π bonding in **5** and stronger π bonding in **6** are reflected by calculated B–P bond orders in these two idealized structures: **5**, 1.35; **6**, 2.01.



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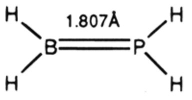

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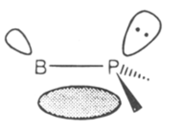

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These theoretical results, as well as standard valence bond hybrid orbital concepts, suggest that the formation of planar, π-bonded phosphinoboranes should be encouraged by placement of electron-donating substituents on phosphorus and electron-withdrawing groups on boron. Although these electronic effects should enhance B–P π overlap through increased P atom lone pair donor and B atom acceptor abilities, they also would enhance acid–base properties of the coordinatively unsaturated fragment and increase the tendency for intermolecular head-to-tail association. As noted above, the standard approach for hindering association employs placement of sterically bulky substituents at the boron and/or phosphorus atoms, and as described in section II, this design has been used effectively by Power and co-workers[19,20] to obtain a number of multiply bonded phosphinoboranes. From an electronic standpoint, it is known that addition of π-donating substituents (e.g., amino groups) at boron reduces its acceptor strength, but such B–N π interactions are expected to compete favorably against B–P π overlap in the same molecule. Therefore, as discussed in the following sections, it is found that B and P atom substituent groups play a crucial role in the elaboration of phosphinoboranes structures and reactivity.

A. Preparation

Several general synthetic routes have been employed in attempts to prepare monomeric phosphinoboranes (eqs 1–3).[19] Lithium halide metathesis

$$X_2B{-}Hal + LiPR'_2 \xrightarrow{-LiHal} X_2B{-}PR'_2 \qquad (1)$$

$$X_2B{-}Hal + Me_3SiPR'_2 \xrightarrow{-Me_3SiHal} X_2B{-}PR'_2 \qquad (2)$$

$$X_2B{-}Hal + HPR'_2 \xrightarrow{-HHal} X_2B{-}PR'_2 \qquad (3)$$

reactions have been used most often since a variety of lithium phosphide salts are easily prepared, and product workup of the hydrocarbon soluble phosphinoboranes is relatively simple. Silane elimination reactions are also straightforward, although they require synthesis of an appropriate silylphosphane precursor. In some instances, the silyl halide Me_3SiHal or silane Me_3SiH elimination process is sluggish, and it must be thermally promoted. This can have a deleterious outcome if the phosphinoborane product is fragile. Direct reactions of boranes with phosphanes that eliminate HHal are also simple on paper, but these reactions often require base promotion or thermal activation.

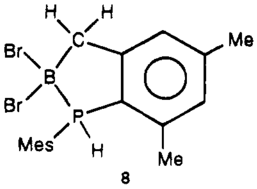
1. Monophosphinoboranes

Although a few monomeric phosphinoboranes were prepared prior to 1986, most were not fully characterized by spectroscopic methods, and none were structurally confirmed by single-crystal X-ray diffraction techniques. Since the reports of the synthesis and structure determinations for Mes_2BPPh_2[9] and Tmp(Cl)BP(H)(Mes),[23] a flurry of activity has resulted in numerous new examples listed in Table 1. As suggested above, these compounds are most often obtained in relatively high yields from metathesis reactions between the appropriate organohaloborane or aminohaloborane and a lithium phosphide reagent. A combination of steric protection, particularly with bulky organic substituents on the smaller boron atom, and electronic influences, especially with π-donating amido groups on the electron deficient boron atom, have been used to hinder head-to-tail association. It is important to point out that sterically bulky ligands are not always innocent. For example, Kar-

Table 1. Structural and NMR Data for Phosphinoboranes, X_2BPY_2

compound	bond length P−B (Å)	sum of angles at P (deg)	$\delta^{31}P$ (J_{PH} (Hz))	$\delta^{11}B$	ref(s)
Mes_2BPPh_2 (**2**)	1.859(3)	339.4	36.7	70.9	9, 21
Mes_2 $BPMes_2$ (**4**)	1.839(8)	360	27.4	82.4	21
$Mes_2BP(^tBu)_2$ (**53**)	1.839(8)	352.0	80.1	61.9	21
	1.843(8)	359.2			
$Mes_2BP(H)(1\text{-}Ad)$ (**61**)	1.897(3)	314.8	0.45	83.8	21
$Mes_2BP(H)(^tBu)$ (**62**)			−4.0 (270)	83.8	19
$Mes_2BP(H)(Ph)$ (**63**)			−41.5 (254)		15
$Mes_2BP(H)(Cy)$ (**64**)			−20.0 (264)		15
$Mes_2BP(H)Mes$ (**65**)			−66.0 (301)		15
$Trip_2BP(H)(^tBu)$			−1.6 (269)	79.7	15
$Mes_2BP(Ph)(SiPh_3)$ (**66**)	1.842(6)	358.2(2)	−35.1	72.0	21
$Mes_2BP(1\text{-}Ad)(SiMe_3)$ (**67**)	1.846(8)	348.7(3)	10.8	66.2	
$^tBu_2BP(^tBu)_2$			6.3	96.3	66
$[Mes_2BP(1\text{-}Ad)]_2$ (**68**)	1.852(9)	359.4	2.8	49.3	16
$[Mes_2BP(Mes)]_2$			−22.3	54.0	16
$^tBu_2BP(SiMe_3)_2$			−189.6	93.5	66
$(9\text{-}BBN)BP(^tBu)_2$			45.2	84.8	66
$(9\text{-}BBN)BP(SiMe_3)_2$			−153.5	87.8	66
$Cy_2BP(^tBu)_2$			33.8	88.3	66
$Tmp(Cl)BP(H)Ar^*$ (**77**)			−98.7	47.6	33
$Tmp(Cl)BP(Me)Ar^*$ (**78**)			−14.6	58.0	33
$Tmp(F)BP(H)Ar^*$			−177.0 (233)	36.5	83
$Tmp(Cl)BP(Me_3Si)Ar^*$			−23.6	62.0	33
$Tmp(Cl)BP(H)Mes$ (**3**)	1.948(3)	307.1(10)			23
$Tmp(Cl)BP(Ph)(SiMe_3)$ (**80**)			−87.9	44	32
$Tmp(Cl)BP(H)(Ph)$ (**81**)			−89.8 (218)	40	32
$Tmp(Cl)BP(H)(CEt_3)$			−88.2 (230)	46.1	52
$^tBu_2N(F)BP(H)(CEt_3)$			−102.5	39.7	56
$^iPr_2N(Br)BP(H)(CEt_3)$			−91.2 (245)	38.5	56
$^iPrN(Cl)BP(H)(CEt_3)$			−98.9 (220)	39.9	84
$Tmp(Cl)BP(H)(Trip)$			−128.7 (238)	45.4	56
$Tmp(F)BP(H)(Trip)$			−149.5 (230)	37.4	56
$Tmp(F)BP(H)[CH(SiMe_3)_2]$			−142.1	37.7	56
$Tmp(Cl)BP(H)(^tBu)$			−52.6 (130)	45.9	83
$^tBu_2N(F)BP(H)(Trip)$			−144.1 (209)	37.9	56
$Me_2NB(Cl)B(NMe_2)[P(H)^tBu]$ (**141**)			−58.9 (224)	40.9	83
				50.0	
$Me_2NB[P(H)^tBu]B(NMe_2)[P(H)^tBu]$ (**142**)			−56.3	50.9	83
$Me_2NB[P(SiMe_3)_2]B(NMe_2)[P(SiMe_3)_2]$ (**145**)			−211.3	52.9	83
$Me_2NB(Cl)P(H)(^tBu)$ (**181**)			−74.7 (213)	40.3	64, 84
$Me_2NB(OEt)P(H)(^tBu)$ (**182**)			−74.7 (234)	33.3	64, 84
$(^iPr_2N)_2BP(SiMe_3)_2$			−232	38.7	61
$(^iPr_2N)_2BPH_2$			−206 (208)	40.9	61
$(^iPr_2N)(Cl)BP(SiMe_3)_2$			−213.3	40.6	66
$(Ph_2N)(Cl)BP(SiMe_3)_2$			−211.6	46.2	66
$Tmp(Cl)BP(SiMe_3)_2$			−179.5	46.4	66
$[(Me_3Si)_2N](Cl)BP(SiMe_3)_2$			−175.8	54.2	66
$(^iPr_2N)(NH_2)BP(SiMe_3)_2$			−245.8	31.2	66
$(^iPr_2N)(N_3)BP(SiMe_3)_2$			−240.0	34.3	66
$(^iPr_2N)(Cl)BPH_2$			−197.9 (209)	39.9	66
			−198.3 (209)		
$(Ph_2N)(Cl)BPH_2$			−204.0 (216)	44.0	66
			−196.6 (216)		
$Tmp(Cl)BPH_2$			−184.1 (210)	44.3	66
			−183.8 (210)		
$[(Me_3Si)_2N](Cl)BPH_2$			−184.3	52.1	66

sch[34] found that the reaction of BBr_3 with $LiPMes_2$ resulted in methyl group C−H bond addition across the P−B bond of the anticipated product $Br_2B{=}PMes_2$. The product **8** therefore contains four-coordinate B and P atoms. The successful synthesis of a number of $X_2BPX'_2$ monomers containing RP(H) and PH_2 groups, on the other hand, indicates that it is not necessary to provide steric or electronic shielding at *both* the B and P atoms in order to isolate the low-coordinate compounds. This has proven pivotal to the synthesis of more complex phosphinoboranes because the primary and secondary phosphane fragments are useful assembly centers for additional substitution reactions. The further impact of substituent group selection on spectroscopic and molecular structure properties is discussed in section III.B.



8

2. Diphosphinoboranes

Further extending the carbon/BP compound analogy, it is expected that diphosphinoboranes would

Table 2. Structural and NMR Data for Diphosphinoboranes $XB(PY_2)_2$ and Triphosphinoboranes, $B(PY_2)_3$

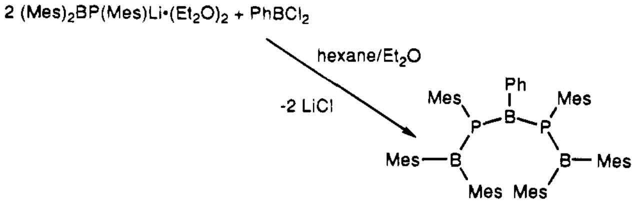
compound	bond length P–B (Å)	sum of angles at P (deg)	$\delta^{31}P$	$\delta^{11}B$	ref(s)
$PhB(PPh_2)_2$ (**9**)					74, 81
$Et_2NB(PEt_2)_2$ (**10**)			−57.4	50.9	43, 49
$Et_2NB(PPh_2)_2$ (**11**)			−37.1	49.1	49
$Me_2NB[P(SiMe_3)_2]_2$ (**12**)			−200		27
$PhB[P(SiMe_3)_2]_2$ (**13**)			−196		27
$MesB(PPh_2)_2$ (**14**)	1.901(2)	318.8	−0.01	30.1	13
	1.879(2)	324.5			
$BrB(PMes_2)_2$ (**15**)	1.82(1)	347.1	−31.2	51.5	34
	1.84(1)	346.7			
$EtOB(PMes_2)_2$ (**16**)			−65.4	55.0	34
$PhB[P(Mes)BMes_2]_2$ (**17**)	1.869(14)		20.6	53.1	22
	1.847(13)			63.6	
	1.859(16)	~360			
	1.874(14)				
	1.879(16)				
	1.839(15)	~360			
	1.850(4)				
	1.891(15)				
$Ph_2NB[P(H)B(N^iPr_2)_2]_2$			−155.4	57.0	61
				41.3	
$^iPr_2NB(PH_2)_2$ (**22**)			−192	48.9	65
$TmpB(PH_2)_2$ (**24**)			−181.3	53.4	65
$(Me_3Si)_2NB(PH_2)_2$ (**25**)			−174.1	68.0	65
$Ph_2NB[P(SiMe_3)_2]_2$ (**26**)	1.896(7)(avg)	~341	−154.5	56.7	65
$Me_2NB[P(H)(CEt_3)]_2$ (**27**)					84
$(Me_3Si)_2NB[P(H)^tBu]_2$ (**28a**)			−34.5	73.2	83
$Et_2NB[P(H)(^tBu)]_2$ (**28b**)			−53.0	49.6	84
$^iPr_2NB[P(H)(^tBu)]_2$ (**28c**)			−54.8	49.2	84
$[B(PEt_2)_3]_2$	2.018(6)		9.0	34.3	25, 26, 5
	ring avg		52.5		
	1.973(7)				
	exo avg				
$B(PMe_2)(PMes_2)_2$ (**29**)			−46.7	61.8	35
			−76.3		
$(Me_3Si)_2NB\{P(H)B(^iPr_2N)[(Me_3Si)_2N]\}_2$ (**69**)	1.918		−70.5	65.0	85
				37.8	
$(Me_3Si)_2NB[P(H)B(^iPr_2N)_2]_2$ (**70**)			−101.4	67.5	85
				37.7	

have a parallel with allyl anion.[13,19] The first diphosphinoborane, $PhB(PPh_2)_2$ (**9**), was obtained by Coates and Livingstone[74,81] in 1961 from a base-promoted HCl elimination reaction between $PhBCl_2$ and Ph_2PH (eq 4). The air-sensitive compound was characterized by infrared spectroscopy and cryoscopic molecular weight analysis in benzene. Shortly thereafter, Nöth and Schrägle[43] reported formation of an aminodiphosphinoborane, $Et_2NB(PEt_2)_2$ (**10**), from a metathesis reaction (eq 5). This air-sensitive compound was also characterized by its cryoscopic molecular weight in benzene. Salt-elimination chemistry was used by Nöth and Sze[49] to form $Et_2NB(PPh_2)_2$ (**11**), and this compound was more fully characterized by ^{11}B and ^{31}P NMR analyses. Fritz and Hölderich[27] described the formation of $Me_2NB[P(SiMe_3)_2]_2$ (**12**) and $PhB[P(SiMe_3)_2]_2$ (**13**) from similar LiCl elimination chemistry with $LiP(SiMe_3)_2$ as the starting phosphide, and these compounds were partially characterized by NMR spectroscopy.

$$PhBCl_2 + 2\,Ph_2PH \xrightarrow[\substack{+2\,Et_3N\\ -2\,Et_3NHCl}]{C_6H_6,\Delta} \underset{\mathbf{9}}{PhB(PPh_2)_2} + \text{polymer} \qquad (4)^{74,81}$$

$$Et_2NBCl_2 + 2\,LiPEt_2 \xrightarrow[-2\,LiCl]{Et_2O} \underset{\mathbf{10}}{Et_2NB(PEt_2)_2} \qquad (5)^{43}$$

Little further effort was given to expanding this chemistry until 1988, but since then several new examples have been reported and are summarized in Table 2. For example, Power[13] reported the metathetical synthesis and detailed characterization of $MesB(PPh_2)_2$ (**14**). Following this report, Karsch and co-workers[34] found that the compounds $XB(PMes_2)_2$ (X = Br (**15**) and OEt (**16**)) are also obtained via metathesis chemistry. In closely related reactions, Power[14] unexpectedly found that the combination of $MesBBr_2$, $PhBCl_2$, and $ThexBCl_2$ with 2 equiv of $LiP(R')H$ (R′ = Ph, Cy, Mes, ^tBu) produce novel boraphosphabenzenes, $(RBPR)_3$, instead of the expected diphosphinoboranes. This chemistry is discussed further in section III.A.2. In a more predictable fashion, Power[22] recently described the 1:1 reaction of a borylphosphide with $PhBCl_2$ that produces **17** (eq 6). Compound **17** is considered an analogue of the organic pentadienyl cation.



17

(6)[34]

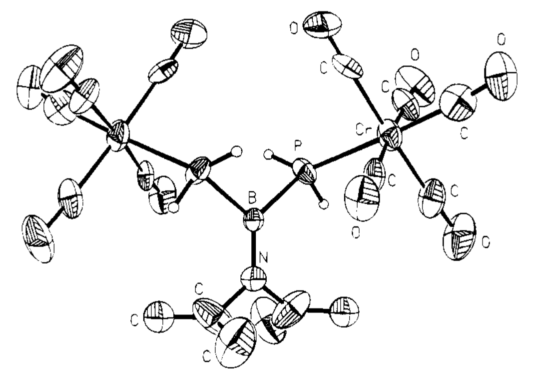
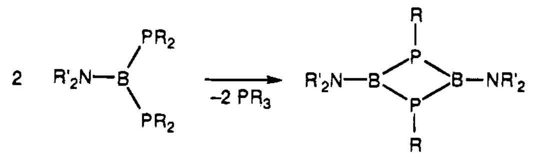


Figure 1. Molecular structure of $^{i}Pr_2NB[P(H)_2Cr(CO)_5]_2$.

Nöth and Paine[56,65] have sought to prepare diphosphinoboranes containing aminoboron substituent fragments, R_2NB, since some of these compounds should be useful reagents for the preparation of ring and cage compounds. In most cases, the compounds are sufficiently labile to decompose readily near room temperature with formation of diphosphadiboretanes **18** (eq 7). The synthetic utility of this reaction is described in more detail in section III.A.1. Diphosphinoaminoboranes that have more than a fleeting existence at 23 °C include $^{i}Pr_2NB[P(SiMe_3)_2]_2$ (**19**), $TmpB[P(SiMe_3)_2]_2$ (**20**), $(Me_3Si)_2NB[P(SiMe_3)_2]_2$ (**21**), $^{i}Pr_2NB(PH_2)_2$ (**22**), $Ph_2NB(PH_2)_2$ (**23**), $TmpB(PH_2)_2$ (**24**), and $(Me_3Si)_2NB(PH_2)_2$ (**25**). NMR data have been used to characterize these compounds, and one compound, $Ph_2NB[P(SiMe_3)_2]_2$ (**26**), has been isolated in pure form and fully characterized including an X-ray crystal structure determination.[65] Compound **22** has been trapped as a metal complex $^{i}Pr_2NB[P(H)_2Cr(CO)_5]_2$, and a view of its molecular structure is shown in Figure 1.[82] A number of diphosphinoboranes containing a secondary phosphane fragment including $Me_2NB[P(H)(CEt_3)]_2$ (**27**) and $(Me_3Si)_2NB[P(H)(^{t}Bu)]_2$ (**28**) have recently been reported.[83,84] Several other related derivatives have been prepared and are in use in BP cage assembly syntheses, as described in section IV.

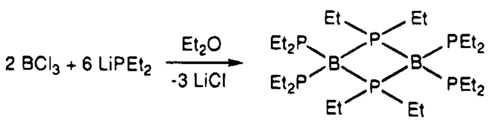


(7)

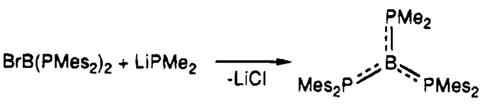
18

3. Triphosphinoboranes

Several attempts[25,26,35] have been made to prepare symmetrical triphosphinoboranes, $(R_2P)_3B$; however, no example has yet been structurally verified by single-crystal X-ray diffraction analysis. The absence of these compounds is probably a consequence of both the unavoidable steric congestion introduced by three large phosphido substituents about the small central boron atom and the availability of alternative reaction paths. For example, Fritz[25,26] reported the 3:1 reaction of $LiPEt_2$ and BCl_3 in ether solution at 50 °C, and no evidence for the formation of $B(PEt_2)_3$ was provided. Instead, a dimeric product was obtained (eq 8) that contains four-coordinate boron and phosphorus atoms. This structure has been subsequently confirmed by single-crystal X-ray diffraction analysis.[51] Apparently, the PEt_2 groups do not provide sufficient steric shielding to block the association. Exploring this point further, Karsch and co-workers[35] recently examined the 3:1 reaction of BBr_3 with $LiP(^{t}Bu)_2$, but no identifiable product was obtained. The 3:1 reaction of BBr_3 with the more bulky phosphide, $LiPMes_2$, on the other hand, produced the target $B(PMes_2)_3$ along with Mes_2PPMes_2 and $BrB(PMes_2)_2$. Unfortunately, this mixture could not be separated, and $B(PMes_2)_3$ (^{31}P δ −50.4) was not obtained in pure form. In a final approach, the diphosphinoborane $BrB(PMes_2)_2$ was allowed to react with $LiPMe_2$ in a 1:1 ratio, and the unique asymmetric triphosphinoborane, $B(PMe_2)(PMes_2)_2$ (**29**) was isolated (eq 9).[35] It was suggested that π conjugation occurs over all three substituents.



(8) [25,26]

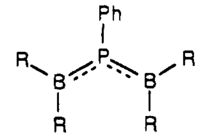


(9) [35]

29

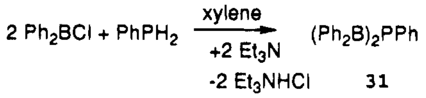
4. Diborylphosphanes

Diborylphosphanes, $(R_2B)_2PR'$ (**30**), should be isoelectronic and isolobal with allyl cation and should therefore have a delocalized valence bond representation. The first diborylphosphane **31** was obtained



30

from the 2:1 combination of Ph_2BCl and $PhPH_2$ (eq 10),[74]but the product was characterized only by

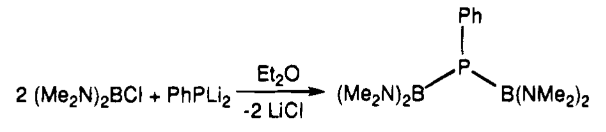


$$2\,Ph_2BCl + PhPH_2 \xrightarrow[\substack{+2\,Et_3N \\ -2\,Et_3NHCl}]{xylene} (Ph_2B)_2PPh \qquad (10)^{74}$$

31

cryoscopic molecular weight measurements in benzene. Nöth and Schrägle[45] subsequently reported metathetical reactions that gave $[(Me_2N)_2B]_2PPh$ (**32**) (eq 11) and $[(Me_2N)(Et_2P)B]_2PPh$ (**33**) (eq 12). Following this, Fritz[27] described formation of **34** (eq 13) by elimination of Me_3SiBr and borylation from a weak adduct.

In more recent studies, the first fully characterized diborylphosphane, $(Mes_2B)_2PPh$ (**35**), was obtained by Power[13] from a metathesis reaction. Nöth and Paine have also recently reported the synthesis of several new diborylphosphanes.[61,85] Illustrative metathesis reaction sequences between $MesBX_2$ and $MesPLi_2$ (eq 14)[84]and $(^{i}Pr_2N)_2BP(H)Li{\cdot}DME$ and



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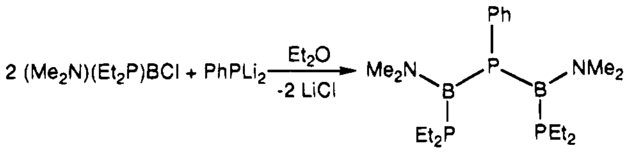
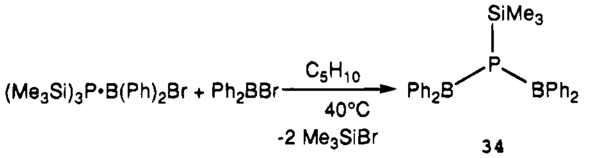
(11)[45]



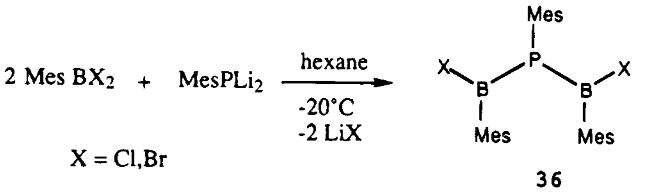
33

(12)[45]



34

(13)[27]



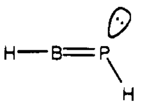
36

(14)[84]

$(R_2N)_2BCl$ or R_2NBCl_2 (Scheme 1)[61] are summarized below. A full summary of diborylphosphane compounds is given in Table 3. It is apparent that many of these compounds have additional functionality, e.g. B−Cl, P−H, P−$SiMe_3$ bonds; therefore, they have considerable use in the synthesis of more complex molecules (see sections III and IV).[85]

5. Boranylidenephosphanes and Borylphosphides

A great deal of the driving force for the recent developments in monomeric phosphinoborane chemistry derives from the quest to prepare and isolate boranylidenephosphanes, $R{-}B{=}\ddot{P}{-}R$, that would be related to linear acetylenes and iminoboranes. Cowley and co-workers[24] have described the results of MO calculations on the model species HBPH in which the two structures **41** and **42** were considered. The minimum-energy species has the bent structure **41**, with a B−P bond distance of 1.756 Å and H−P−B and P−B−H bond angles of 94.5° and 175.0°, respectively. The linear form **42** lies ~23 kcal/mol higher in energy than the bent form, and the dimerization energy of **41** is −54 kcal/mol. Kölle[53] has reported similar general findings for the hypothetical molecule H_2NBPCH_3 for which the calculated dimerization energy is −90 kcal/mol with an activation energy of only 5 kcal/mol. Not surprisingly then, numerous attempts to prepare and isolate monomeric boranylidenephosphanes have been unsuccessful, and



41

42

Scheme 1

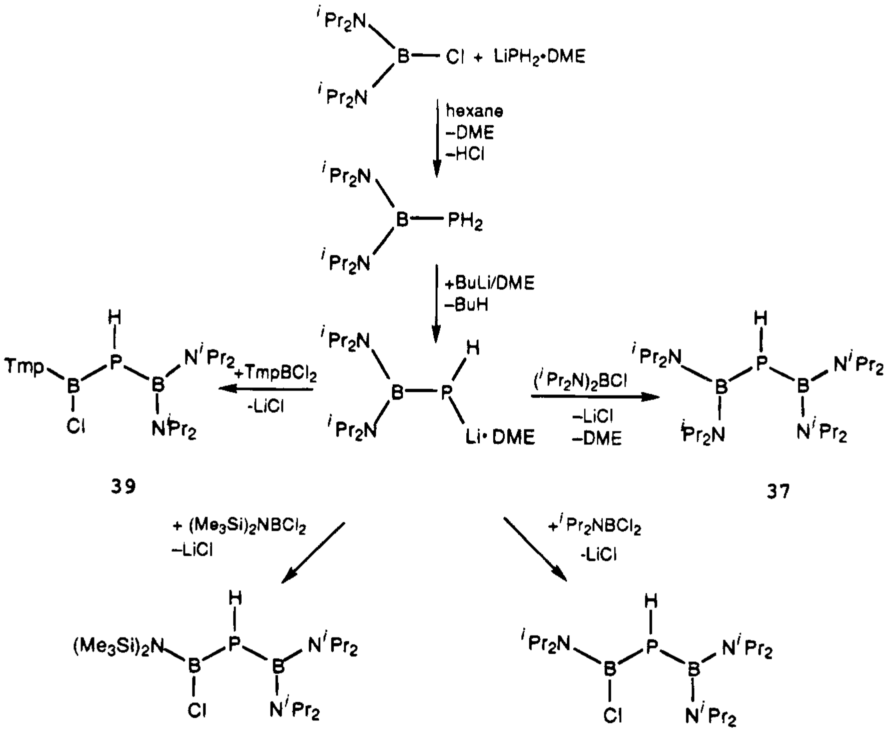
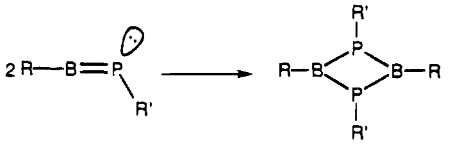


Table 3. Structural and NMR Data for Diborylphosphanes

compound	bond length P–B (Å)	sum of angles at P (deg)	$\delta^{31}P$	$\delta^{11}B$	ref
$(Ph_2B)_2PPh$ (**31**)					74
$[(Me_2N)_2B]_2PPh$ (**32**)					45
$[(Me_2N)(Et_2P)B]_2PPh$ (**33**)					45
$(Ph_2B)_2PSiMe_3$ (**34**)					27
$(Mes_2B)_2PPh$ (**35**)	1.871(2)	~360	60.1	47.8	13
$[MesB(Cl)]_2PMes$ (**36a**)	1.853(4) 1.859(4)	354.3	13.8	65.8	84
$[MesB(Br)]_2PMes$ (**36b**)			31.4	63.0	84
$[(^iPr_2N)_2B]_2PH$ (**37**)			−163.5	40.7	61
$[(^iPr_2N)_2B][(^iPr_2N)B(Cl)]PH$ (**38**)			−170.0	40.7 38.8	61
$[(^iPr_2N)_2B][TmpB(Cl)]PH$ (**39**)			−143.2	46.1 38.5	61
$[(^iPr_2N)_2B][TmpB(NH_2)]PH$			−159.5	41.3	61
$[(^iPr_2N)_2B][(Me_3Si)_2NB(Cl)]PH$ (**40**)			−136.3	53.3 38.5	61
$[TmpB(Cl)][(^iBu_2N)_2B]PH$			−156.8	46.4 37.7	82
$[(Me_3Si)_2NB(Cl)][(^iBu_2N)_2B]PH$			−150.8	53.7 37.2	82
$[TmpB(Cl)][(^iBu_2N)(Me_3Si)_2NB]PH$			−117.4	45.0 39.1	82
$[(Me_3Si)_2NB(Cl)][(^iPr_2N)(Me_3Si)_2NB]PH$			−107.6	51.7 37.9	82

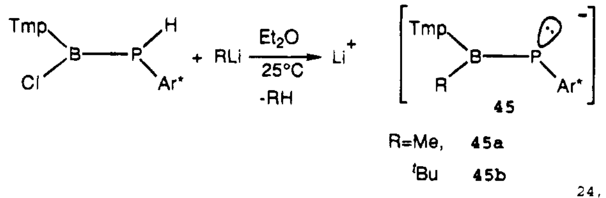
instead the dimeric diphosphadiboretanes **43** have been obtained (eq 15).



43

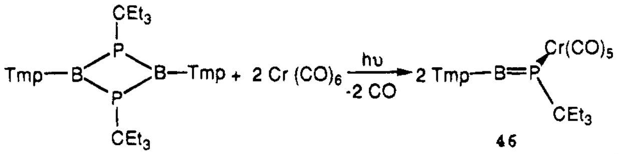
(15)

It is logical to expect that steric congestion at either the phosphorus atom or especially the boron atom might result in a reversal of this dimerization reaction. In an effort to accomplish this outcome, Cowley and co-workers[24] prepared a sterically congested diphosphadiboretane $(TmpBPAr^*)_2$ (**44**). When this compound was heated *in vacuo* at 250 °C and the resulting vapors were analyzed by EI-MS and HRMS, the highest observed mass peak corresponded to monomeric TmpB=PAr*. Efforts to isolate or trap the monomer from pyrolysis streams were unsuccessful. Attempts were also made to isolate the monomer from the reaction of TmpB(Cl)P(H)Ar* with MeLi and ^{t}BuLi, but boranylphosphides **45** were obtained instead (eq 16). Simultaneously, Couret and co-workers[33] described the same reaction scheme at −78 °C with ^{t}BuLi, and they detected the phosphide anion $[Tmp(^tBu)BPAr^{*-}]$ (**45b**) along with diphosphadiboretane $[TmpBPAr^*]_2$ (**44**) in a 70:30 ratio. They suggested that the anion might form by attack of ^{t}BuLi on the incipient boranylidenephosphane. In related chemistry, Kölle[83] found that TmpB(F)P(H)-Ar* does not dehydrohalogenate with the more bulky bases $NaN(SiMe_3)_2$ or $LiN(SiMe_3)(^tBu)$.



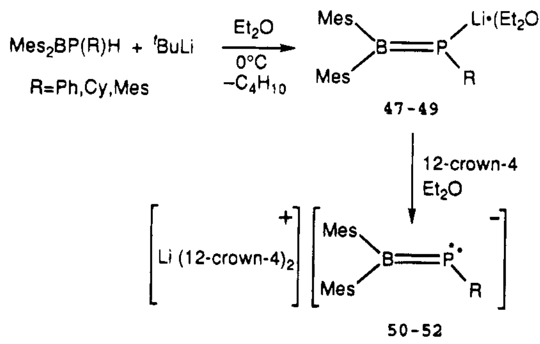
(16)[24,33]

An obvious conclusion from these results is that the Tmp and Ar* substituents do not impart sufficient kinetic stabilization to allow isolation of the target boranylidenephosphanes, if they are formed at all. Instead, they either undergo "self-trapping" via dimerization or addition reactions with R^-. In order to explore both of these points further, Nöth and co-workers[50] examined the reactions of several metal carbonyl fragments with diphosphadiboretanes under thermal and photochemical activation conditions. The majority of the reactions produced metal carbonyl complexes of the diphosphadiboretanes, and these results are described in section III.C.4. In one case (eq 17),however, the transient species TmpB=P-(CEt_3) was trapped on a $Cr(CO)_5$ fragment.[59] The complex was isolated, and its molecular structure is discussed in section III.B.



(17)[59]

Reasoning that the Tmp group provides significant competitive B–N π overlap that would reduce potential B–P π overlap, Power and co-workers[10,15,21] alternatively examined the reaction of several bulky organoborylphosphanes, $R_2BP(H)R'$ with ^{t}BuLi (eq 18). The novel solvated lithium boranylphosphides **47**–**49** and **53**–**56** were initially isolated, and several were converted to unsolvated 12-crown-4 complexes **50**–**52**. The structural characterization of these species indicates that the B–P bond has considerable *double-bond* character. Subsequently, a number of aminoborylphosphides including **57**–**60** have been reported.[61,85] All of these compounds have been prepared by action of an organolithium reagent on



(18)[15,21]

the corresponding borylphosphane. A summary of presently known borylphosphides is provided in Table 4 and some of their chemistry is described in sections III and IV.

B. Structural Characterization

Virtually all of the monomeric phosphinoborane compounds described above have been obtained as pure, air-sensitive liquids, oils, or crystalline solids, and they have been compositionally characterized by elemental analysis and/or by EI or FAB mass spectroscopic analyses. Those compounds that contain primary or secondary phosphane fragments usually display two (A′ and A″) or one infrared P−H stretching frequency, respectively. These bands fall in the region 2400−2200 cm^{-1}. Where the data are available, they tend to mirror the subtle shifts in P atom hybridization induced by the attached substituent groups. These hybridization changes are also indicated by ^{31}P chemical shifts and $^{1}J_{PH}$ values.

It is expected that ^{11}B, ^{31}P, ^{13}C, and ^{1}H NMR spectroscopy should provide a wealth of structural information on phosphinoboranes. In practice, a good deal of information can be extracted; however, the quadrupolar characteristics of the ^{11}B nucleus and the asymmetric local fields in these molecules usually result in broad ^{11}B NMR resonances. Consequently, the hybridization diagnostic *one-bond* B−P coupling constants are rarely observed. Nonetheless, the boron resonances (Tables 1−4) typically fall in the three-coordinate boron shift region,[86] and within this region, the shifts are largely governed by the nature of the directly attached alkyl, aryl, amido, halo, and alkoxy substituent groups.

The ^{31}P NMR shifts for the monomeric phosphinoboranes are most strongly affected by the electronic nature of the substituents and the phosphorus atom hybridization. In general, compounds with organic substituents on trivalent P atoms have shifts in the range 0−80 ppm. Introduction of one or two electron-donating H or Me_3Si substituents typically moves the chemical shift significantly upfield. The introduction of an electropositive boryl group provides a deshielding effect on the phosphorus chemical shift. Those compounds having P−H bonds show $^{1}J_{PH}$ values generally larger than in PH_3 ($|^{1}J_{PH}| = 182$ Hz), related primary ($|^{1}J_{PH}| = 150-210$ Hz), or secondary ($|^{1}J_{PH}| = 180-230$ Hz) organophosphanes. This is normally indicative of increased s character in the P−H bond which in turn suggests that the geometry about the P atom in the phosphinoborane compounds is usually flatter than in the related organophosphanes. By comparing ^{31}P chemical shifts in a *closely* related series of compounds (e.g., Mes_2BPMes_2 (**4**) (δ 27.4), $(MesBPMes)_3$ (**116**) (δ 40.4), $(Mes_2B)_2PPh$ (**35**) (δ 60.1), and $PhB[P(Mes)BMes_2]_2$ (**17**) (δ 20.6)), Power suggests[22] that the relative extent of π delocalization in B−P bond networks can be estimated from ^{31}P chemical shift data. For example, in the compounds listed above, larger positive (downfield) chemical shift values parallel greater B−P π delocalization. It remains to be shown that ^{31}P NMR shift trends in other series of compounds can be used to estimate the extent of B−P π delocalization.

Power and co-workers[21,22] have also made extensive use of variable-temperature ^{11}B, ^{31}P, ^{13}C, and ^{1}H NMR spectroscopy to deduce barriers to hindered rotation. These results have in turn been used to estimate the varying degrees of π delocalization in the various B−P interactions. Finally, in a few cases, ^{7}Li NMR data for several lithium borylphosphides have been obtained.[61,65,85] Typically, the resonances are relatively broad at room temperature, but they sharpen dramatically between 0 and −40 °C. At these low temperatures for the compounds evaluated, $^{7}Li-^{31}P$ splitting patterns are consistent with dimeric structures in solution.

Table 4. Structural and NMR Data for Borylphosphides

compound	bond length P−B (Å)	sum of angles at P (deg)	twist angle B/P planes (deg)	$\delta^{31}P$	$\delta^{11}B$	ref
Tmp(Me)BP(Ar*)(Li) (**45a**)				72		24
Tmp(^{t}Bu)BP(Ar*)(Li) (**45b**)				85.9		24
[Mes$_2$BP(Ph)Li(Et$_2$O)$_2$] (**47**)				73.1	65.4	10
[Mes$_2$BP(Cy)Li(Et$_2$O)$_2$] (**48**)	1.832(6)	357.7	3.8	70.5	65.6	10
[Mes$_2$BP(Mes)Li(Et$_2$O)$_2$] (**49**)	1.823(7)	359.9	11.7	55.5	63.7	10
[Li(12/4)$_2$][Mes$_2$BP(Ph)] (**50**)				103.6		10
[Li(12/4)$_2$][Mes$_2$BP(Cy)] (**51**)				113.6		10
[Li(12/4)$_2$][Mes$_2$BP(Mes)] (**52**)	1.835(13)		0.0	91.3		10
[Mes$_2$BP(^{t}Bu)Li(Et$_2$O)$_2$]				104.3	62.5	15
[Ph$_2$BP(^{t}Bu)Li(Et$_2$O)$_2$]				97.6	64.8	15
[Trip$_2$BP(^{t}Bu)Li(Et$_2$O)$_2$] (**53**)	1.836(2)	356.1	33.3	113.2	58.9	15
[Mes$_2$BP(1-Ad)Li(Et$_2$O)$_2$] (**54**)	1.823(8)	357.4	13.8	90.4	85.7	21
[Mes$_2$BP(SiMe$_3$)Li(THF)$_3$ (**55**)	1.833(6)	357.7	22	−49.2	71.6	15
{TripB[P(H)Mes]P(Mes)Li(Et$_2$O)$_2$} (**56**)	1.927(3)	306.7	24.3	32.0	64.0	15
	1.810(4)	359.4	18.6	−117.0		
[(^{i}Pr$_2$N)$_2$BP(H)Li(DME)]$_2$ (**57**)	1.901(5)			−213	46.8	61
[(^{i}Pr$_2$N)$_2$BP(SiMe$_3$)Li(THF)]$_2$ (**58**)			dimeric	−257.3	45.3	61
[(^{t}Bu$_2$N)$_2$BP(H)Li(DME)]$_2$ (**59**)				−247.8	47.4	85
[(^{i}Pr$_2$N)B[(Me$_3$Si)$_2$NBP(H)Li(DME)]$_2$ (**60**)				−183.2	45.0	85

Single-crystal X-ray diffraction analyses have proven very helpful for both general structure verification and for revealing the detailed differences in B–P interactions in this wide range of monomeric phosphinoboranes. In all cases, the primary structural features of interest are the B–P distance, the deviation from planarity for the phosphorus atom geometry, and the degree of twisting of B-substituent and P-substituent planes about the B–P bond axis. The B–N bond distance in the aminoborylphosphanes is also important and diagnostic of the degree of competition between B–N and B–P π overlap. Power and co-workers[19–21] have discussed in detail the trends in the structural parameters for the organo-substituted phosphinoboranes, and we expand here on those discussions. Pertinent data are listed in Tables 1–4.

In general, Power concludes that, in compounds containing planar B and P atoms, a B–P bond length less than 1.9 Å signifies some degree of B–P π overlap.[21] For example, in the neutral monophosphinoboranes **2**, **4**, **53**, **66**, and **67** containing Mes$_2$B groups and silyl and/or organic substituents on the P atom, the B–P bond distances span the range 1.839–1.859 Å. These distances are significantly shorter than the range of distances associated with B–P single bonds, 1.9–2.0 Å. On the other hand, one compound containing a Mes$_2$B group, **61**, and less sterically demanding substituents (H and 1-Ad) on the phosphorus atom displays a long B–P distance of 1.897(3) Å. Further, in the compounds **2**, **4**, **53**, **66**, and **67**, the P atom geometry is nearly planar, as shown by the sums of angles about the phosphorus atom ranging from 339 to 360°. The sum of angles in **61**, however, is 314.8°. These data are in agreement with the theoretical pictures mentioned previously.[75–79] In the nonplanar form (ground state) of H_2BPH_2, the calculated B–P bond distance is 1.901 Å, and the out-of-plane angle at phosphorus is 70°. The planar form (excited state), on the other hand, has a calculated B–P bond distance of 1.807 Å. Lest it be thought that B–P bond shortening arises only from improved π-overlap as the P atom geometry is flattened, Power[19–21] reminds us that this geometric compression also enhances σ overlap through enhanced rehybridization toward idealized sp^2. Indeed, it is not clear whether the planar geometry in the silyl-substituted derivative **66** arises because of enhanced electron density on the P atom when bonded to SiPh$_3$ relative to Ph or because of the greater steric bulk and lower inversion barrier associated with a silylphosphane. In this vein, replacement of Ph in **66** with the less bulky 1-Ad group in **67** gives little change in B–P distance, but the sum of angles about phosphorus decreases slightly. In contrast, the structure of the monophosphinoborane **3** containing the amino group Tmp shows a dramatically elongated B–P bond distance, 1.948(3) Å, and a pyramidal phosphorus atom environment. Clearly, B–N π overlap goes a long way toward satisfying the coordinative and electronic unsaturation at boron at the expense of less competitive B–P π overlap.

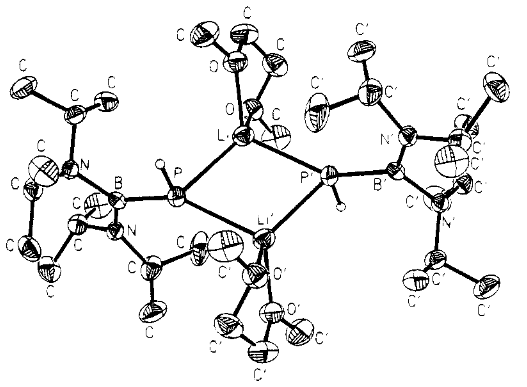
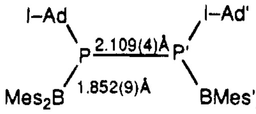


Figure 2. Molecular structure of $[(^i\text{Pr}_2\text{N})_2\text{BP(H)Li(DME)}]_2$ (**57**).

The molecular structures of the borylphosphides (Table 4) offer further confirmation of the bonding picture summarized above. The structures fall into two groups: borylphosphide–lithium etherate complexes containing direct P–Li bonds and borylphosphide–crown ether chelated Li$^+$ ion pair complexes. It is important to note that most lithium organophosphides, in solution and the solid state, exist as associated species, typically dimers, but **47–49** and **53–55** are clearly monomeric in the solid state. This is consistent with the phosphorus atom lone pair being given to B–P π bonding and not to Li–P bridging interactions between monomer units. The monomeric, ether-solvated species all have short B–P bond distances, 1.823(7) to 1.836(2) Å, and planar or near-planar phosphorus atom geometries. Extraction of the Li$^+$ cation from **49** with 12-crown-4 results in no significant change in structural parameters for **52**. This suggests that the Li–P interactions in the ether-solvated monomeric complexes are relatively weak and stereochemically insignificant.

The lithium salt **56** of {TripB[P(H)Mes]P(Mes)Li(Et$_2$O)$_2$} is particularly noteworthy. The B–P(H)Mes bond length is relatively long, 1.927(3) Å, while the distance in the phosphide unit B–PMes$^-$, 1.810(4) Å, is the second shortest B–P bond distance. The structure of only one Li salt of an aminoborylphosphide **57** has been determined. Not surprisingly, the ^{i}Pr$_2$N group provides significant π overlap to boron; consequently, the B–P bond is weakened. This is clearly evidenced by the relatively long B–P bond distance, 1.901(5) Å. In addition, the compound is dimeric, as shown in Figure 2.



The molecular structure of the 1,2-diboryldiphosphane, [Mes$_2$BP(1-Ad)]$_2$ (**68**) is also particularly interesting.[16] The molecule has a 2-fold rotation axis perpendicular to the P–P′ bond, planar P and B atom geometries with a dihedral angle of 25.5°, a large (70.5°) dihedral angle between the P and P′ planes, and a relatively short P–B bond distance. This molecule appears to be analogous to butadiene since the B–P bond distance and small B–P dihedral angle suggest a significant degree of B–P π orbital interaction. The large twist angle about the P–P′ bond, however, weakens this analogy. The structure differs from that of normal diphosphanes, R$_2$P–PR$_2$, that typically have a more pyramidal P atom geometry

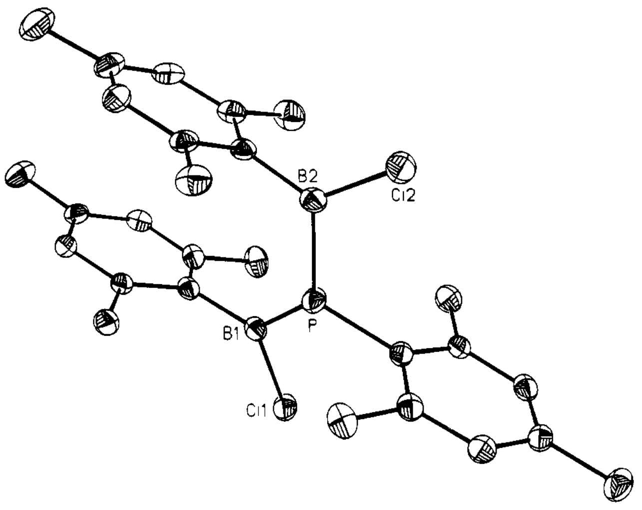


Figure 3. Molecular structure of $[MesB(Cl)]_2PMes$ (**36a**).

with bond angles significantly less than tetrahedral. This indicates less s character than in idealized sp^3 hybridization. Consequently, it is appropriate to consider the P−P′ bond in **68** as a single bond formed by overlap of sp^2 hybrid orbitals. The increased s character in the P−P σ bond is likely responsible for the intermediate distance compared to the average P−P distance in diphosphanes, 2.22 Å, and in diphosphenes, 2.03 Å.

The molecular structure of the diborylphosphane $(Mes_2B)_2PPh$ (**35**) shows that the molecule has a 2-fold axis, planar boron and phosphorus atom geometries, and a moderately short B−P bond distance, 1.871(2) Å. These features are consistent with the stated analogy between **35** and the allyl cation,[13] and it will be interesting to follow if reactivity parallels develop between these organic and inorganic systems. The molecular structure of $[MesB(Cl)]_2PMes$ (**36a**) has also been determined,[84] and a view is shown in Figure 3. With the presence of an electron-withdrawing group on the boron atoms, it might be expected that the B−P bond distance in this molecule might be shorter than in **35**. This is indeed the case, $B{-}P_{avg}$ = 1.856 Å, and the P atom is nearly planar.

The molecular structure of the related diphosphinoborane $MesB(PPh_2)_2$ **14** is dramatically different from **35** because it features longer B−P bonds and a pyramidal P atom geometry. This suggests that the B−P π overlap is reduced, and the B−P hybrid orbitals are more sp^3 like. Replacement of the Mes group with the electron-withdrawing substituent bromine, as in $BrB(PMes_2)_2$ (**15**), shortens significantly the B−P bond distance and increases the sum of angles at the phosphorus atom (~347°). Further, in the compound $PhB[P(Mes)BMes_2]_2$ (**17**), the P atom geometries are essentially planar and the PhB−P bond distances are 1.869(14) Å and 1.847(13) Å. These features may be attributed to the addition of the electropositive $BMes_2$ group to the PMes fragments. Another extreme is provided by the structures of $(Me_3Si)_2NB\{P(H)B(N^iPr_2)[(Me_3Si)_2N]\}_2$ (**69**) and $(Me_3Si)_2NB[P(H)B(N^iPr_2)_2]_2$ (**70**).[85] In both cases, the phosphorus atom geometries are pyramidal, and the P−B bond distances are all in the single-bond range. This is consistent with the absence of B−P π overlap. The boron atom electron deficiency is satisfied instead by strong B−N π overlap, as indicated by short B−N bond distances.

The molecular structure of the boranylidenephosphane complex **46** is especially interesting. The PBN unit is nearly linear (176.1(3)°), and the CNC plane of the Tmp ring and the CrPC(butyl) plane are nearly orthogonal (96.0°). The B−P bond distance, 1.743(5) Å, is the shortest yet reported, and the sum of bond angles about phosphorus is 360°. These facts are consistent with the presence of significant π overlap in this B−P bond. In addition, the B−N bond distance, 1.339(5) Å, is short, and the NB unit is almost linear (176.1(3)°). This indicates that these atoms are also engaged in π overlap. These structural features indicate that the boranylidenephosphane fragment is stabilized against dimerization by the $Cr(CO)_5$ fragment.

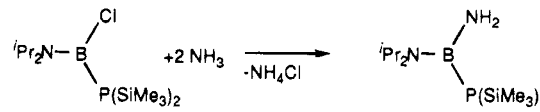
C. Reaction Chemistry

The reactivity of monomeric phosphinoboranes has been scarcely studied, and much of the work reported was accomplished before the reactants were fully characterized. It can be expected that monomeric phosphinoboranes, because of their tendency to adopt the single B−P bond structure (e.g., **5** over **6**), will be much more reactive than alkenes and somewhat more reactive than monomeric aminoboranes. In addition, some different reaction patterns are expected. In practice, phosphinoboranes are modestly air and moisture sensitive and usually stable at room temperature. For the most part, the boron−alkyl, boron−aryl, phosphorus−alkyl, and phosphorus−aryl bonds are robust; therefore, reactivity is centered on the phosphorus lone pair density, the boron-acceptor orbital, and at boron−halogen, phosphorus−hydrogen, phosphorus−silicon, boron−nitrogen, and boron−phosphorus bonds. The known reactivity patterns are summarized below.

1. Behavior toward Bases

a. Addition Compounds and Nucleophilic Substitution. With all of the intense effort to sterically shield the Lewis acidic boron atom, little effort has been made to test the residual difunctional P atom donor and B atom acceptor chemistry of phosphinoboranes. Of course, the fact that sterically underprotected phosphinoboranes readily dimerize indicates that there is some Lewis acid and base character in these monomer units. Metal carbonyl coordination chemistry also indicates that the phosphorus atom in these fragments retains Lewis donor character. Still, this area has not been fully explored, and the chemistry is worthy of greater attention.

Several studies of nucleophilic substituent group displacements have been accomplished. For example, B−Cl and B−Br bonds undergo substitution with amines, azide, carbanions, and hydride (eqs 19–23).[45,61,65,66]



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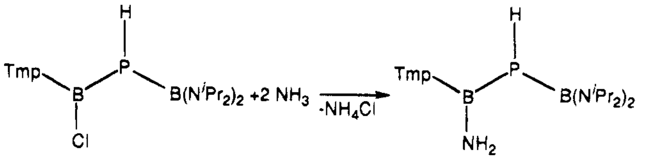

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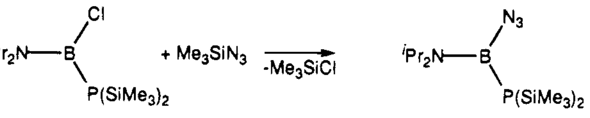

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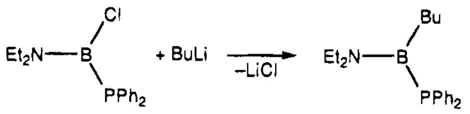

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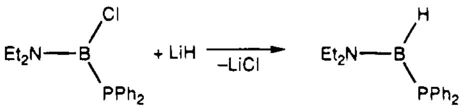
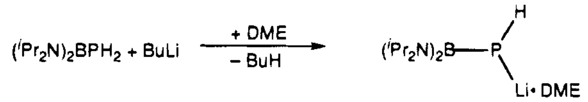


(23)[45]

b. Deprotonation. Phosphinoboranes containing primary or secondary phosphane functionality are easily deprotonated by strong bases such as BuLi, ^{t}BuLi, MeLi, R_2NLi, and H_2PLi. Indeed, these reactions provide access to synthetically important borylphosphides whose reactivity is briefly described below and in sections III and IV. One example of deprotonation chemistry is shown (eq 24). Of course, if the boron fragment is susceptible to nucleophilic displacement, then that process can take place along with (eq 25) or without phosphane deprotonation (eq 26). Double deprotonation of a primary borylphosphane apparently does not occur; at least the resulting dianions have not been isolated.



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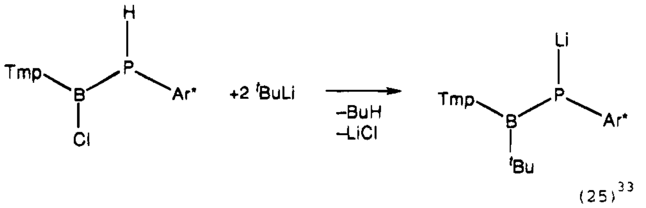

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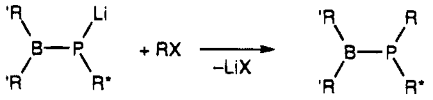
${}^tBu_2B\text{-}P(SiMe_3)_2 + {}^tBuLi \longrightarrow LiP(SiMe_3)_2 + {}^tBu_3B$ (26)[66]

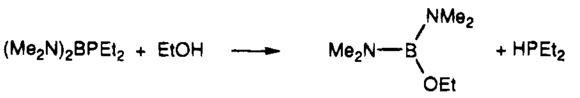
The reaction chemistry of borylphosphide anions has been explored in several studies.[61–66] As expected, they are excellent nucleophiles, and they produce a number of new phosphinoboranes (eq 27) and diborylphosphanes (Scheme 1). They also provide access to new ring and cage compounds described in sections III and IV.



(27)

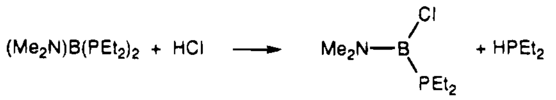
2. Behavior toward Acids

a. Reactions with Protic Acids. In general, the combination of a phosphinoborane and a protic acid such as HCl, HBr, H_2O, ROH, and RNH_2 leads to cleavage of a B–P bond (eqs 28 and 29). When a diphosphinoborane is allowed to react with a protic source with careful control of the reagent stoichiometry, new monophosphinoboranes are obtained (eq 30). As expected, the reaction of the novel $Cr(CO)_5$ complex **46** with HCl in Et_2O generates a borylphosphane complex (eq 31).



(28)[46]

$(Me_2N)_2BPEt_2 + H_2NC_6H_5 \longrightarrow (Me_2N)_2B\text{-}N(H)C_6H_5 + HPEt_2$ (29)[46]



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(31)[59]

b. Reaction with Lewis Acids. The phosphorus lone pair on aminophosphinoboranes should be available for coordination with classical Lewis acids. Surprisingly, the addition of B_2H_6 to $(Me_2N)_2BPEt_2$ does not result in isolation of a phosphaneborane adduct.[46] Instead, the adduct, if formed, undergoes rearrangement (eq 32). Addition of BCl_3 to $(Me_2N)_2BPEt_2$ also gives rise to redistribution (eq 33). More recently, the reaction of $H_3B{\cdot}THF$ with (9-BBN)P(^{t}Bu)$_2$ has been studied,[66] and a complex reaction ensues that gives several products including $[H_2BP({}^tBu)_2]_2$.

$(Me_2N)_2BPEt_2 + 2\,B_2H_6 \longrightarrow 1/3\,(Et_2PBH_2)_3 + 2\,Me_2NB_2H_5$ (32)[46]

$2\,(Me_2N)_2BPEt_2 + 2\,BCl_3 \longrightarrow 2\,(Me_2N)_2BCl + (Cl_2BPEt_2)_2$ (33)[46]

3. Behavior as Ligands

Although the addition of classical Lewis acids to phosphinoboranes tends to give rearrangement products, the reactions with metal carbonyls are generally well behaved, and borylphosphane metal carbonyl complexes are obtained in good yields. Some examples are summarized in Table 5. In each case, the phosphorus lone pair is coordinated to the metal

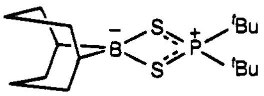
Table 5. Metal Carbonyl Complexes of Phosphinoboranes

compound	bond length P−B (Å)	ν(CO) (cm^{-1})	$\delta^{31}P$	$\delta^{11}B$	ref
$(Me_2N)_2BPPh_2[Cr(CO)_5]$		2057, 1934			49
		1951,			
$(Me_2N)_2BPPh_2[Mo(CO)_5]$		2068, 1943			49
		1957			
$(Me_2N)_2BPPh_2[W(CO)_5]$		2066, 1933			49
		1947			
$Et_2NB(PEt_2)_2[Cr(CO)_5]_2$		2079, 2056, 1950, 1942	−17.4	45.7	49
		1934			
$Et_2NB(PPh_2)_2[Cr(CO)_4]$		2016, 1930, 1910, 1904		38.9	49
$Et_2NB(PPh_2)_2[Mo(CO)_4]$		2028, 1936, 1920, 1911		40.7	49
$Et_2NB(PPh_2)_2[W(CO)_4]$		2024, 1930, 1911, 1904		41.6	49
$(Me_2N)_2B_2(PPh_2)_2[Cr(CO)_4]$		2016, 1930, 1911, 1903		46.2	49
$(Me_2N)_2B_2(PPh_2)_2[Mo(CO)_4]$		2027, 1936, 1919, 1911			49
				46.4	49
$(Me_2N)_2B_2(PPh_2)_2[W(CO)_4]$		2024, 1930, 1912, 1904			49
				47.5	
$TmpBP(CEt_3)[Cr(CO)_5]$	1.743(5)		−45.3	62.9	55
$[(^iPr_2N)_2B]_2P(H)[Cr(CO)_5]$	2.044	2052, 1926	−157.9	38.1	61
	2.032				
$[(^iPr_2N)_2B][TmpB(Cl)]P(H)[Cr(CO)_5]$	1.961	2056, 1973	−109.5	44.5	61
	2.034	1932		36.2	
$(^iPr_2N)B(Cl)P(SiMe_3)_2[Cr(CO)_5]$		2054, 1971, 1929	−189.9	40.2	65
$(^iPr_2N)B(Cl)P(SiMe_3)[W(CO)_5]$		2066, 1983, 1931	−185.5	39.4	65
$TmpB(Cl)P(H)(CEt_3)[Cr(CO)_5]$			−15.7	41.3	64
$TmpB(Cl)P(H)(^tBu)[Cr(CO)_5]$			3.6	39.7	64

carbonyl fragment, and the phosphane acts as a simple two-electron donor.

4. Oxidation and Nucleophilic Displacement Reactions

The addition of S_8 to two phosphinoboranes has been examined. With $(Me_2N)_2BPEt_2$, the reaction products $(Et_2N)_4B_2$ and $Et_4P_2S_5$ show complete degradation of the phosphinoborane B−P unit.[46] With (9-BBN)$P(^tBu)_2$, a novel cyclic product **71** is obtained.[66] As observed with organophosphanes, addition of methyl iodide to phosphinoboranes typically gives phosphonium salts (eqs 34 and 35).



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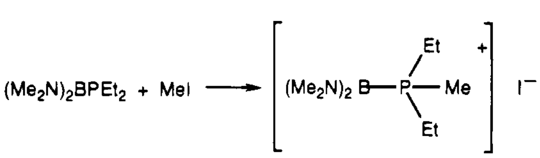

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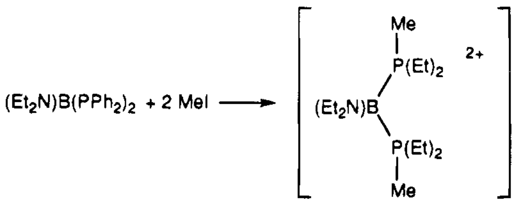

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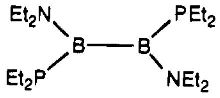
5. Reduction Reactions

Phosphinoboranes containing a B−Cl bond might be expected to undergo reductive coupling to give B−B bonded dimeric species. For example,[45] the reaction of Na/K alloy with $Et_2NB(Cl)PEt_2$ gives **72**. Although this chemistry is rich for aminohaloboranes, R_2NBHal_2, few other examples utilizing phosphinoboranes have been reported.



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6. Thermal Chemistry

It has recently been shown that the monomeric organophosphinoboranes $^tBu_2BP^tBu_2$ and $Cy_2BP^tBu_2$ undergo a dehydroboration reaction when warmed in hexane solution or heated neat *in vacuo*, and tetraorganophosphanylboranes $[^tBu(H)BP^tBu_2]_2$ and $[Cy(H)BP^tBu_2]_2$ are formed.[66] The related compound $[Thex(H)BP^tBu_2]_2$ is obtained without isolation of the intermediate monomeric phosphinoborane. Each of the dimeric compounds is obtained as a mixture of *cis* and *trans* isomers.

III. Cyclic Phosphinoboranes

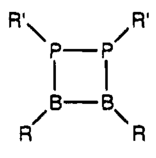
It was pointed out in the Introduction that monomeric phosphinoboranes, without steric or electronic shielding, readily associate and form four-, six-, and eight-membered ring compounds with four-coordinate boron and phosphorus atoms.[70] These compounds, of course, have parallels with saturated cyclic organic compounds, e.g., cyclobutane, cyclohexane, and cyclooctane, as well as with saturated aminoboranes $(R_2NBR_2)_n$ (n = 2, 3, 4). Several new examples of these compounds have been prepared in the last few years; however, with the exception of the compounds described in section II.C.6.,[66] that chemistry is not reviewed here. Instead, in the following section, attention is focused on the much less studied cyclic phosphinoboranes that contain three-coordinate boron and phosphorus atoms.

A. Preparation

The majority of cyclic three-coordinate phosphinoboranes have been prepared from elimination reactions involving boron halide and organophosphane or organophosphide reagents. The formation of stable elimination byproducts (e.g., PH_3, $P(SiMe_3)_3$, RPH_2, HCl, HBr, LiCl, LiBr, NaCl, KCl, Me_3SiCl, and Me_3SiBr) typically helps drive the reactions, and the cyclic products are usually obtained in good yields.

1. Four-Membered B_2P_2, B_3P, and BP_3 Rings

There are two basic classes of B_2P_2 rings that can be prepared: 1,2,3,4-diphosphadiboretanes (**73**) and 1,3,2,4-diphosphadiboretanes (**43**). Only one example of a 1,2,3,4-diphosphadiboretane has been reported, and it was obtained from the combination of $[K(^tBuP)]_2$ and $[(Me_2N)(Cl)B]_2$ (eq 36).[30] Prior to 1986, there was also only one report of a 1,3,2,4-diphosphadiboretane, and it was prepared via $(Me_3Si)_3P$ elimination from a diphosphinoborane (eq 37).



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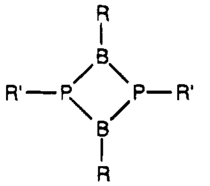

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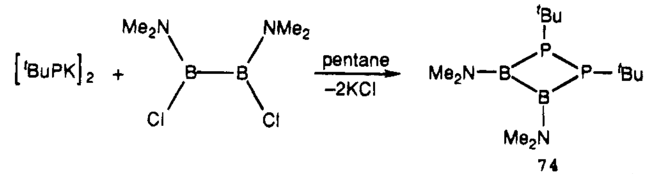

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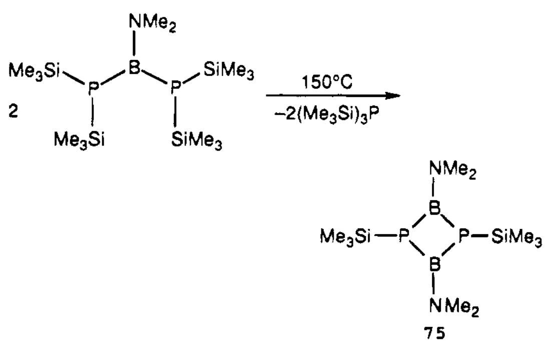

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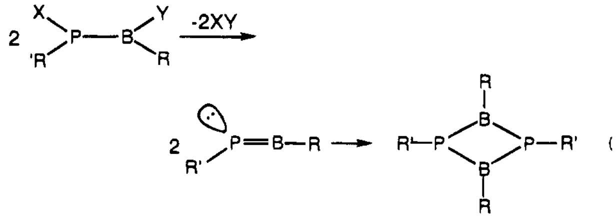
(37)[27]

Since 1986, the intense search for boranylidenephosphanes, RB=PR′, has led to reports of the formation of numerous 1,3,2,4-diphosphadiboretanes. Although the mechanistic details are not yet confirmed, it may be anticipated that some of these compounds form by head-to-tail dimerization of transient boranylidenephosphanes generated in 1,2-elimination chemistry from monomeric phosphinoboranes (eq 38) or from loss of phosphane from 2 equiv of diphosphinoboranes. Examples of 1,3,2,4-diphosphadiboretanes that have been isolated are summarized in Table 6. Cowley and co-workers,[23] for example, examined the reaction of a 1:1 mixture of $MesPLi_2$ and MesP(H)Li with $TmpBCl_2$ from which $(TmpBPMes)_2$ (**76**) was isolated. It appears that $MesPLi_2$ serves as a dehydrohalogenation promoter. The intermediate monomeric phosphinoborane, TmpB(Cl)P(H)Mes (**3**), was isolated as well in this study from the reaction of $TmpBCl_2$ with LiP(H)Mes. Cowley and co-workers,[24] using a sequential LiCl/Me_3SiCl double elimination scheme (eq 39), described the formation of $(TmpBPAr^*)_2$ (**44**) without isolation of the intervening phosphinoborane. It was noted that **44** was not obtained by dehydrohalogenation of the related phosphinoborane TmpB(Cl)P(H)Ar* (**77**) with MeLi or ᵗBuLi. These reactions instead were observed to give the borylphosphides $[Tmp(R)B-PAr^{*-}]$ (**45a** and **45b**) described earlier in section II.A.5 (eq 16). At the same time, a related study by Couret and co-workers[33] of the dehydrohalogenation of TmpB(Cl)P(H)Ar* (**77**) with ᵗBuLi in THF solution at −78 °C showed that both the borylphosphide anion $[TmpB(^tBu)PAr^{*-}]$ (**45**) and the 1,3,2,4-diphosphadiboretane (**44**) were formed in a ~70:30 ratio. Couret and co-workers[32] then demonstrated that $(TmpBPPh)_2$ (**79**) could be obtained by at least three elimination reactions (eqs 40−42). The formation of the phosphinoborane intermediates **80** and **81** (eq 41 and 42) was confirmed by isolation of these species.



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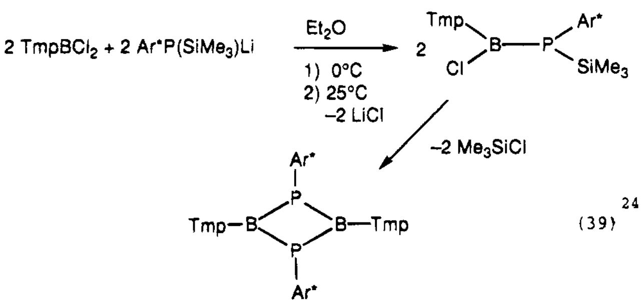

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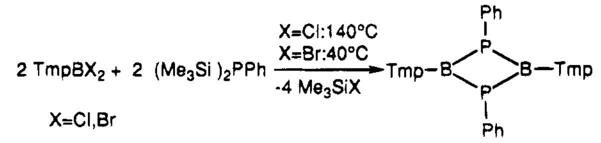
(39)[24]



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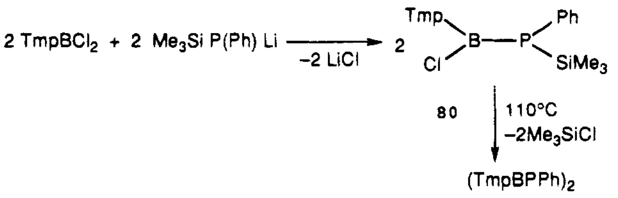
(40)[32]



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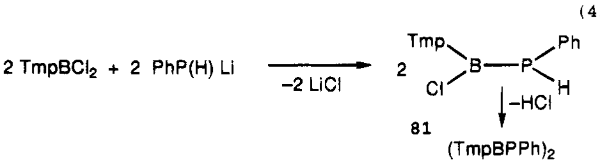


(42)[32]

Table 6. Cyclic B_2P_2, B_3P, and BP_3 Rings

compound	bond length P–B (Å)	sum of angles at P atom (deg)	$\delta^{31}P$	$\delta^{11}B$	refs
$(PhBPSiMe_3)_2$					27
$(Me_2NBP^tBu)_2$ (**74**)			−23.2	50	30
$(Me_2NBPSiMe_3)_2$ (**75**)			153		27
$(TmpBPMes)_2$ (**76**)	1.916(3)				23
$(TmpBPAr^*)_2$ (**44**)	1.96(2)		−92.8		33
$(TmpBPPh)_2$ (**79**)			−59.7	43	32
$(ThexBPMes)_2$ (**82**)	1.898(5) 1.896(7)	331.3	−70.7	95.1	14
$[MesBP(1\text{-}Ad)]_2$ (**83**)	1.900(2)	328.9	−69.8		19
$[MesBP(^tBu)]_2$ (**84**)	1.897(2)	328.8	10.6	86.2	17, 20, 68
$(TmpBPCEt_3)_2$ (**85**)	1.924(2)(avg)	329.2	−20	66.1	52, 84
$(^tBu_2NBPCEt_3)_2$			−14.4	67.0	84
$(TmpBP^tBu)_2$ (**86**)				63.2	
$[TmpBPTrip]_2$ (**87**)			−101.0	55.0	56
$[TmpBPCH(SiMe_3)_2]_2$ (**88**)			−83.4	59.0	56
$(Ph_2NBPSiMe_3)_2$ (**89**)			−122.6	58.0	56, 65
$(^iPr_2NBPSiMe_3)_2$ (**90**)	1.951(5)(avg)	281.8(avg)	−133.6	50.6	56
$(TmpBPSiMe_3)_2$ (**91**)	1.956(12)(avg)	287.9(avg)	−55.0	60.8	56
$(^tBu_2NBPTrip)_2$	1.923(5)(avg)	301.9(avg)	−94.4	55.4	56
$[Me_2NBP^tBu]_2$ (**92**)	1.927(3)(avg)	309	−46.8	50.2	56, 64
$[(Mes_3Si)_2NBP^tBu]_2$ (**93**)			−2.2	68.3	56
$(^iPr_2NBPH)_2$ (**94**)	1.931(3)(avg)	312.4	−162.8	47.1	65, 84, 87
$(TmpBPH)_2$ (**95**)	1.913(4) 1.934(4)		−127.2	50.8	65
$[(Me_3Si)_2NBPSiMe_3]_2$			−63.3	69.1	65
$TmpBP(H)(Tmp)BPSiMe_3$			−129.3	50.7	65
			−108.8		56, 65
$(Et_2NBP^tBu]_2$ (**219**)			−49.1	48.9	64
$(^iPr_2NBP^tBu)_2$	1.919(10) 1.939(9)	313.5	−48.0	45.8	64, 84
$(^iPr_2NBPCEt_3)_2$	1.93(1)(avg)	318.1	−68.9	55.1	64
$\{TmpBPB[N(^iBu)_2]_2\}_2$ (**98**)			−81.1	58.4 36.0	85
$\{[(Me_3Si)_2NBPB[N(^iBu)_2]_2\}_2$ (**99**)			−66.2	70.4 34.2	85
$TmpBP(H)B(Tmp)PB(Cl)(^iPr_2N)$ (**104**)			−98.9 −107.8	51.0 39.0	62
$^iPr_2NBP(H)B(N^iPr_2)PB(Cl)(^iPr_2N)$ (**105**)					62
$^iPr_2NBP(H)B(N^iPr_2)PB(Cl)(Me_3Si)_2N$ (**106**)			−77.8 −151.4	52.0 47.0	62
$^iPr_2NBP(H)B(N^iPr_2)PB(Cl)(Tmp)$ (**107**)			−108.1 −126.9	50.3 39.3	62
$^iPr_2NBP(H)B(N^iPr_2)PSiMe_2Ph$ (**108**)			−149.9 −154.0	48.3	67
$TmpBP(H)B(Tmp)PSiMe_2Ph$ (**109**)			−107.2 −130.6	50.6	67
$^iPr_2NBP(H)B(N^iPr_2)PSiPh_2Cl$ (**110**)			−144.6 −149.7	47.8	67
$TmpBP(H)B(Tmp)PSiPh_2Cl$ (**111**)			−102.6 −128.1	49.8	67
$TmpBP(H)B(Tmp)PSiMe_2Cl$ (**112**)			−106.0 −123.6	49.0	67
$(Me_3Si)_2NBP(^tBu)P(^tBu)P^tBu$ (**113**)			6.9	64.7	83
$Me_2NB(Me_2N)B(Me_2N)BP^tBu$ (**114**)			−71.4 4.2		84
$[(^tBu)_3C_6H_2OBP(^tBu)]_2$ (**115**)			−38.1	58.3	84
$(^tBu)_3C_6H_2OBP(^tBu)(Ar^*)BP(^tBu)$ (**116**)			−7.5	81.8 56.3	84

Power and co-workers[14,18,20] have recently succeeded in isolating 1,3,2,4-diphosphadiboretanes **82**–**84** that do not have π-donating amino groups. In each case, the compounds have been obtained by reaction of an organodihaloborane with 2 equiv of LiP(H)R′ (eq 43).

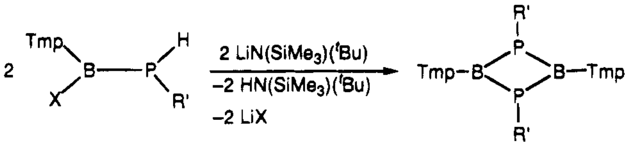
Nöth and Paine have explored syntheses for 1,3,2,4-diphosphadiboretanes as part of their search for

$$2\,RBCl_2 + 4\,LiP(H)R' \xrightarrow[-2\,H_2PR']{-4\,LiCl} (RBPR')_2 \qquad (43)^{14,20}$$

R/R′: Mes/1-Ad, Thex/Mes, Mes/ᵗBu

82 **83** **84**

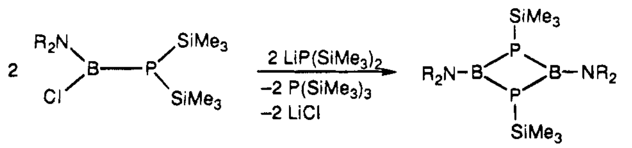
RB=PR′ species and for precursors of more complex boron−phosphorus compounds. In some cases, the ring compounds were prepared by dehydrohalogenation of an isolated phosphinoborane $R_2NB(Cl)P(H)R'$ or directly from a dihaloborane without isolation of the intermediate phosphinoborane. Some of this chemistry is illustrated below (eqs 44−47). In the reactions described in eqs 45−47, it is likely that, in each case, a diphosphinoborane is first formed that decomposes and leaves free phosphane and a boranylidenephosphane. The latter dimerizes and gives the observed 1,3,2,4-diphosphadiboretane (eq 48). In all cases, the amino group on boron is relatively large, and it is this substituent that appears to largely control the formation of the dimeric species. The formation of six-membered rings containing smaller amino groups is described in section III.A.2.



R′ = Ar*, CEt₃, ᵗBu, Trip, CH(SiMe₃)₂,

44 **85** **86** **87** **88**

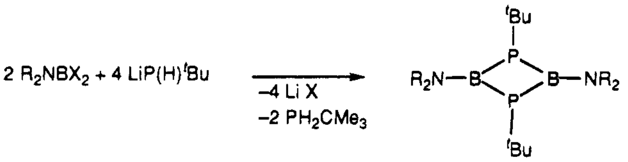
(44)[56]



R₂N = NPh₂, NⁱPr₂, Tmp

89 **90** **91**

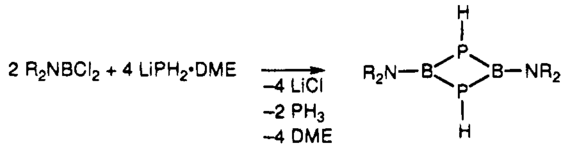
(45)[56]



R₂N = Me₂N, (Me₃Si)₂N

92 **93**

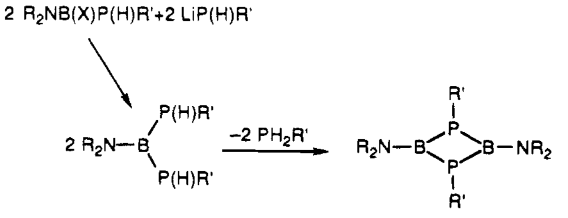
(46)[56,64]



R₂N = ⁱPr₂N, Ph₂N,Tmp

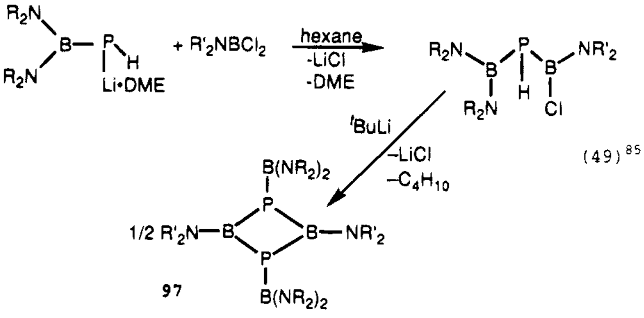
94 **95** **96**

(47)[65]



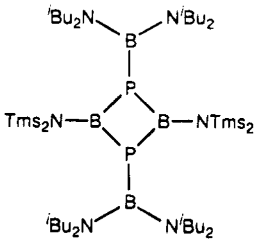
(48)[65]

It was also found that dehydrohalogenation reactions on selected diborylphosphanes $(R_2N)_2BP(H)B(Cl)NR'_2$ give cyclocondensations with formation of P-diborylated 1,3,2,4-diphosphadiboretanes **97** (eq 49).[85] Two specific compounds that have been isolated are **98** and **99**. It should be noted that this reaction is not typical for all R_2N or R'_2N groups. Although only a few combinations have so far been explored, at least two other reaction pathways have been discovered. For example, dehydrohalogenation of $TmpB(Cl)P(H)B(N^iPr_2)_2$ (**39**) gives rise to a novel C−H activation of one ⁱPr group, and a P-borylated four-membered PBNC ring compound **100** is obtained (eq 50).[63] When diborylphosphanes **101** and **40** are employed, acyclic B_3P_2 chain compounds **102** and **103** are obtained (eqs 51 and 52).[85]

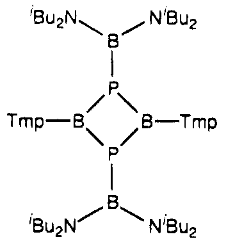


97

(49)[85]



98



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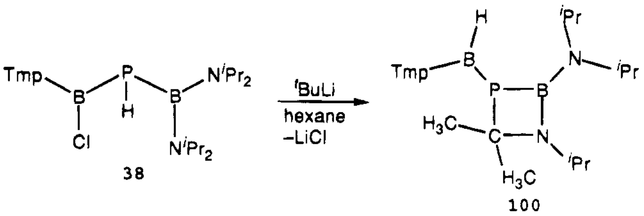
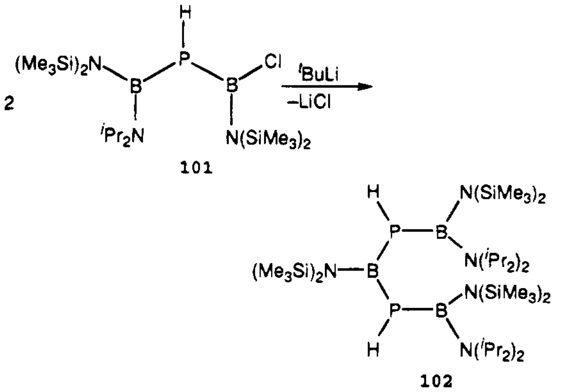


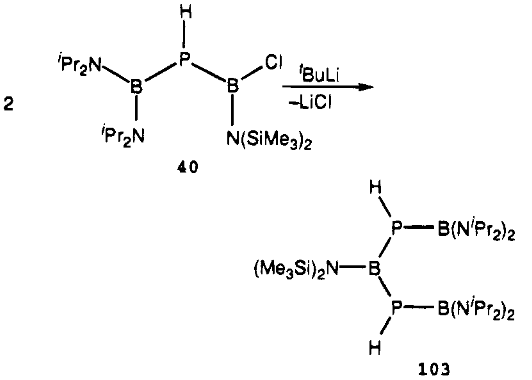
38 **100**

(50)[63]

It might be expected that many other 1,3-di-P-substituted 1,3,2,4-diphosphadiboretanes could be obtained by double deprotonation of **94** and **96** with

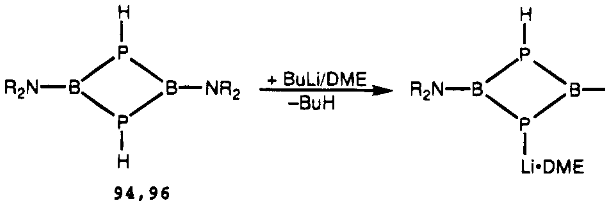


(51)[85]



(52)[85]

a strong base (eq 53) followed by addition with 2 equiv of RX, R_3SiX, or EX_n species. It is found that monodeprotonation does occur easily, for example, with BuLi, but the double deprotonation does not take place to a significant extent.[62,67] One species that reacts like a dianion $[(Tmp)BP]_2^{2-}$ is obtained from the reaction of $(TmpBPH)_2$ with Na/K alloy.[67] The nature of this species is not yet known, and the double deprotonation has not been achieved with other diphosphadiboretanes. The addition reactions on the cyclic phosphides are generally facile, and a number of new substituted rings **104–112** have been isolated.[62,67] These are summarized in Table 6.



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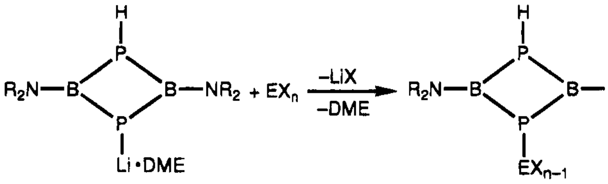
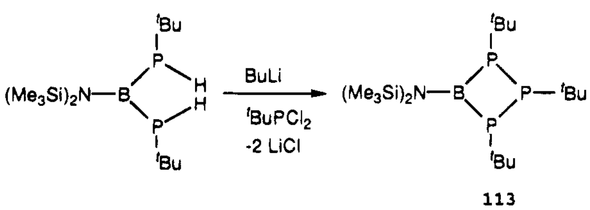


(54)

Appropriately substituted diphosphinoboranes should also serve as useful precursors to BP_3 rings; however, only one such compound has been isolated. Kölle[83] has noted that combination of $(Me_3Si)_2NB$-$[P(^tBu)H]_2$ with BuLi followed by addition of $^tBuPCl_2$ gives the four-membered ring **113** (eq 55). Work is in progress in our groups to expand this chemistry. Similarly, aminohalotriboranes $Me_2N(X)B(Me_2N)B$-$(Me_2N)BX$ should serve as useful reagents for the formation of B_3P rings, and Linti[84] has reported formation of **114** from such a reaction (eq 56).



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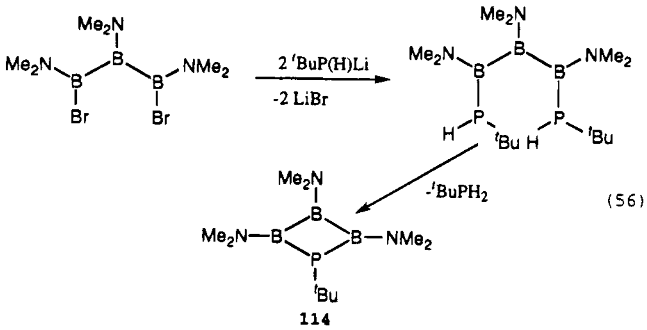
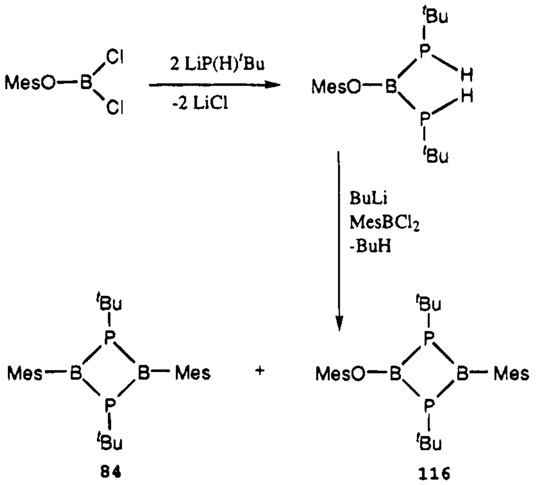


(56)

It is worth pointing out that only two diphosphadiboretanes with alkoxy groups on the boron atoms have been reported. Linti[84] noted that reaction of $^tBu_3C_6H_2OBCl_2$ with 2 equiv of $LiP(H)^tBu$ gave the symmetrical four-membered ring $[^tBu_3C_6H_2OBP^tBu]_2$ (**115**) in low yield, and the molecule was not isolated. However, when the intermediate diphosphinoborane was deprotonated with BuLi and the anion combined with $MesBCl_2$ (eq 57), the asymmetrically substituted B_2P_2 ring **116** and the known symmetrical ring **84** were obtained.



(57)[84]

2. Six-Membered B_3P_3 and B_4P_2 Rings

A six-membered boron–phosphorus ring compound containing three-coordinate B and P atoms is potentially isostructural and electronically related to benzene and borazine. The first example of this class of compounds, $(MesBPCy)_3$ (**117**), was reported by Power

Table 7. Cyclic B_3P_3 Rings

compound	bond length P–B (Å)	sum of angles at P Atom (°)	$\delta^{31}P$	$\delta^{11}B$	ref(s)
$(MesBPCy)_3$ (**113**)	1.839(6)avg	~360	51.9	52.6	11
$(MesBP^tBu)_3$ (**114**)			60.5	53.9	14
$(MesBPPh)_3$ (**115**)	1.842(4)(avg)	~360	42.5	52.5	14
$(MesBPMes)_3$ (**116**)			40.4	49.6	14
$(PhBPMes)_3$ (**117**)			14.5	50.2	14
$(^iPr_2NBPH)_3$ (**118**)			−162		65, 84
$(Me_2NBPH)_3$ (**119**)					65
$(Et_2NBPH)_3$ (**120**)					65
$[(Mes_3Si)_2NBPH]_3$ (**121**)	1.928(10)(avg)		−68.3	68.4	65

and co-workers[11] in 1987. Following this report, several more examples **118–121** were found as products of the reactions of aryl boron halides with lithium phosphides (eq 58).[14] Further examples of

$$RBX_2 + 2\,LiPHR' \xrightarrow[-H_2PR']{-2\,LiX} 1/3\,(RBPR')_3 \qquad (58)$$

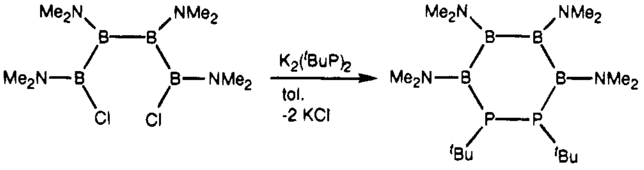
R/R' =Mes/Cy, Mes/^{t}Bu, Mes/Ph, Mes/Mes, Ph/Mes

117 118 119 120 121

these products are summarized in Table 7. It was noted by Power that for the aryl- and alkyl-substituted compounds, a planar, six-membered ring geometry is favored with less bulky substituent groups R and R′. With slightly more bulky R/R′ combinations, the same reaction produces four-membered 1,3,2,4-diphosphadiboretanes (eq 43, R/R′ Mes/1-Ad, Thex/Mes, and Mes/^{t}Bu) or a mixture of four- and six-membered rings.[14,20]

In a parallel fashion, Nöth and Paine observed that the reactions of aminodichloroboranes, R_2NBCl_2 R = Me, Et, and Me_3Si with 2 equiv of $LiPH_2{\cdot}DME$ also produce six-membered rings **122–125**.[65] In these cases, however, the rings are not planar. When R = tmp and Ph, four-membered rings **95** and **96** (eq 47) are obtained and when R = ^{i}Pr, a mixture of four- and six-membered rings is produced. With the exception of the trimer containing large $N(SiMe_3)_2$ groups, these results suggest that the smaller amino groups also favor the six-membered ring structure. Of course, electronic factors may contribute to the adoption of one ring size over another. The structures of these molecules are discussed further in section III.B.

One example of the potential family of B_4P_2 ring compounds has been reported by Linti[84] from the combination of an aminohalotetraborane and $K_2(^tBu)_2P_2$ (eq 59). Further developments in this B_4P_2 ring family will probably require new synthetic approaches since the availability of other starting materials for this reaction are limited.

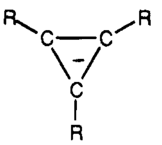


126

(59)[84]

3. Three-Membered B_2P and BP_2 Rings

Cyclopropenyl anion **127** is a well-known 4π electron, antiaromatic, organic compound that is expected to be related to the generalized diphosphaborinane **128**. Boron–phosphorus compounds of this class have been reported by Baudler and Marx[28,29] from the [2 + 1] cyclocondensation of $(K^tBuP)_2{\cdot}(THF)_{0.5}$ and aminodichloroboranes (eq 60). The isolated examples of **128** (**129–135**) are summarized in Table 8. Several of these compounds are reported to dimerize with formation of compounds **136–140**.



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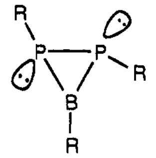
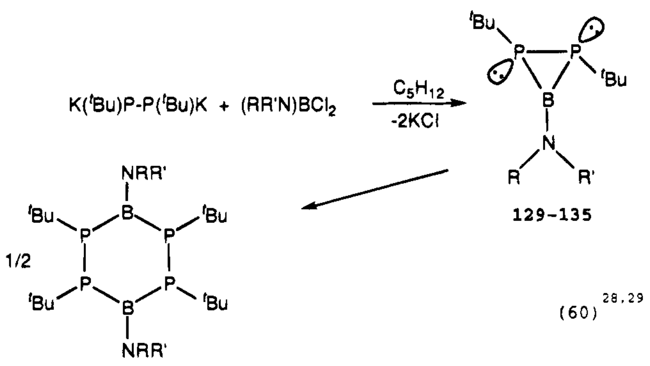


128

Table 8. Structural and NMR Data for Cyclic Phosphinoboranes $(XP)_2BY$, Their Dimers $(XP)_4(BY)_2$, and $XP(BY)_4$

compound	bond length P–B (Å)	sum of angles at P atom (deg)	$\delta^{31}P$	$\delta^{11}B$	ref
$(^tBuP)_2BN(^iPr)_2$ (**129**)			−159.2	50.7	28
$(^tBuP)_2BNEt_2$ (**130**)	1.892(2) 1.893(2)	268.3 268.2	−152.5	52.6	29
$(^tBuP)_2BNPh_2$ (**131**)			−151.4	59.5	29
$(^tBuP)_2BN(Me)(^tBu)$ (**132**)			−139.8 −168.8	51.2	29
$(^tBuP)_2BN(Me)(^nBu)$ (**133**)			−145.7 −150.3	53.2	29
$(^tBuP)_2BN(Me)(Cy)$ (**134**)			−147.3 −157.0	52.8	29
$(^tBuP)_2BN(Me)(Ph)$ (**135**)			−141.8 −155.4	60.6	29
$(^tBuP)_4(BNEt_2)_2$ (**136**)			−54.7	46.6	29
$(^tBuP)_4(BNPh_2)_2$ (**137**)			−38.8	~50	29
$(^tBuP)_4[BN(Me)(Bu)]_2$ (**138**)			−52.7	48.2	29
$(^tBuP)_4[BN(Me)(Cy)]_2$ (**139**)			−54.2	48.6	29
$(^tBuP)_4[BN(Me)(Ph)]_2$ (**140**)			−48.6	~50	29
$[Me_2NB(NMe_2)BP^tBu]_2$ (**144**)	1.990 1.960		−76.9	54.3	83
$Me_2NB(Me_2N)B(Me_2N)B(Me_2N)BP^tBu$ (**146**)	1.958(3)	314.1	−34.2	59.2 54.5	84



129–135

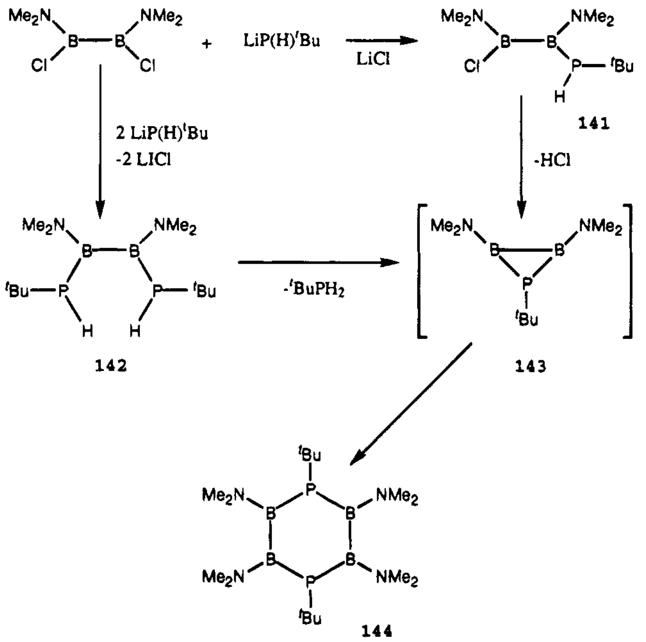
136–140

(60)[28,29]

These species are also listed in Table 8. The precise nature of the dimeric structure has not been determined; however, it is assumed to be a six-membered ring.[29]

An attempt has been made to prepare a B_2P ring as illustrated in Scheme 2.[83] In this case, however,

Scheme 2[83]



141

142

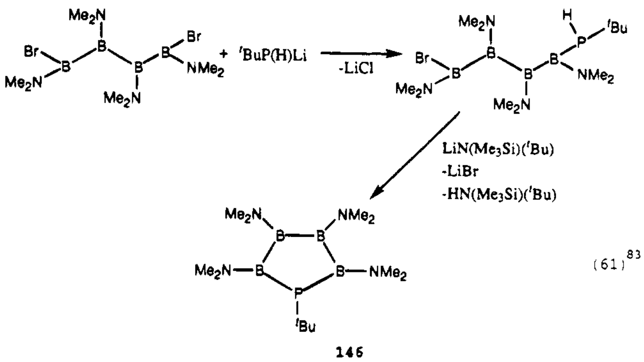
143

144

the monomeric three-membered ring **143** was not isolated. Instead, the dimer, a B_4P_2 compound, **144** was obtained, and the six-membered ring structure was confirmed by single-crystal X-ray diffraction analysis. A similar reaction of $Me_2NB(Cl)-B(Cl)NMe_2$ with 2 equiv of $LiP(SiMe_3)_2$·THF gave a phosphinoborane $Me_2NB[P(SiMe_3)_2]B(NMe_2)[P(SiMe_3)_2]$ (**145**) that did not cyclize.[83]

4. Five-Membered B_4P Ring System

At this time, five-membered B_xP_y ring compounds are rare since they are represented by only one well-characterized example. Kölle[83] has obtained **146** in good yield from addition of ᵗBuP(H)Li to an aminobromotetraborane (eq 61) followed by base-induced dehydrobromination. The intermediate acyclic phosphinoborane was isolated and characterized as well: ^{11}B δ 54.1; ^{31}P δ −64.0. The molecular structure of **146** is discussed in section III.B. No other derivatives of the B_4P system have been reported, so the generality of this approach remains to be demonstrated.

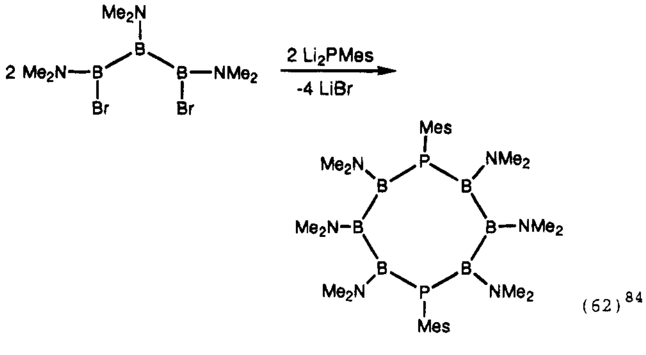


146

(61)[83]

5. Eight-Membered B_6P_2 Rings

Only one example of the potential eight-membered ring family has so far been obtained. Compound **147** is isolated from the reaction of an aminobromotriborane with Li_2PMes (eq 62).[84] It was expected that a four-membered B_3P ring would be obtained; however, in this case, the "dimer" system appears to be favored. The molecular structure of **147** is described in section III.B.

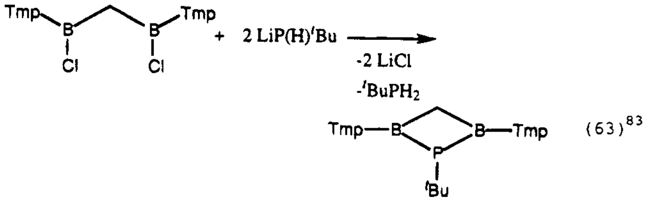


147

(62)[84]

6. Ring Systems Containing Additional Atoms, $B_nP_m(EX)$

Several boron–phosphorus ring compounds containing one or more heteroatom (E) or heteroatom group (EX) have been prepared, and some examples are summarized in Table 9. For example, Kölle[83] has described an interesting sequential salt and phosphine elimination process that results in a B_2PC four-membered heterocycle **148** (eq 63). This result stimulated a series of studies by Kölle[83] and Linti[84] of the reactions of bis(lithio-*tert*-butylphosphino)methane with a series of boron halide reagents. This chemistry is summarized in Scheme 3.



148

(63)[83]

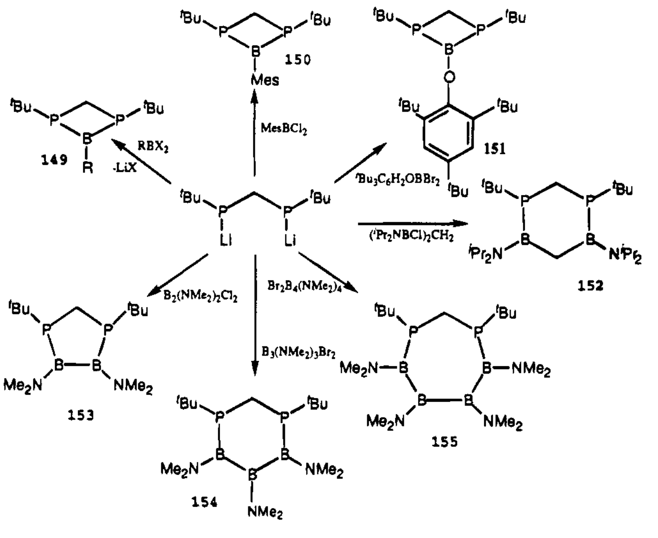
Table 9. Structural and NMR Data for B_nP_m(EX) Rings

compound	bond length P–B (Å)	sum of angles at P atom (deg)	δ^{31}P	δ^{11}B	ref
$\mathrm{Br_2BP(Mes)(H)[Me_2C_6H_2]CH_2}$ (**8**)			−5.33		34
$\mathrm{TmpBCH_2B(Tmp)P{}^tBu}$ (**148**)			−32.2	52.7	83
$\mathrm{{}^tBuPCH_2P({}^tBu)B(NMe_2)BNMe_2}$ (**141**)			−68.8	54.7	83
$\mathrm{(Me_3Si)_2NBP({}^tBu)CH_2P({}^tBu)}$ (**149a**)			39.9	71.5	83
$\mathrm{TmpB({}^tBu)CH_2P({}^tBu)}$ (**149b**)			29.6	55.1	83
$\mathrm{Me_2NBP({}^tBu)CH_2P{}^tBu}$ (**149c**)			12.5	48.5	84
$\mathrm{{}^tBu(Bz)NBP({}^tBu)CH_2P{}^tBu}$ (**149d**)			9.6	51.3	84
$\mathrm{MesBP({}^tBu)CH_2P{}^tBu}$ (**150**)	1.884(avg)	309(avg)	16.1	76.0	84
$\mathrm{{}^iPr_2NBCH_2B({}^iPr_2N)P({}^tBu)CH_2P{}^tBu}$ (**152**)			−49.4	47.2	84
$\mathrm{Me_2NB(Me_2N)B(Me_2N)BP({}^tBu)CH_2P{}^tBu}$ (**154**)	1.968(avg)		−40.8	56.3	84
$\mathrm{Me_2NB(Me_2N)B(Me_2N)BP({}^tBu)CH_2P{}^tBu}$ (**154**)			−46.1	57.2	84
$\mathrm{{}^tBuPCH_2CH_2P({}^tBu)BNMe_2}$ (**156a**)			−6.8	60.3	84
$\mathrm{{}^tBuPCH_2CH_2P({}^tBu)BN(SiMe_3)_2}$ (**156b**)			−10.3	80.3	84
$\mathrm{PhPCH_2CH_2P({}^tBu)BNMe_2}$ (**157**)			−59.6	56.1	84
$\mathrm{{}^iPr_2NBC(H)C(H)B(N{}^iPr_2)PPh}$ (**158**)	1.942(9)	295.1	−124.6	47.7	38
$\mathrm{Et_2NBC(H)C(H)B(NEt_2)PSiMe_3}$ (**159a**)			−254.1	48.7	41
$\mathrm{{}^iPr_2NBC(H)C(H)B(N{}^iPr_2)PSiMe_3}$ (**159b**)			−241	47.4	41
$\mathrm{Et_2NBC(H)C(H)B(NEt_2)PH}$ (**160a**)			−230.4	47.2	41
$\mathrm{{}^iPr_2NBC(H)C(H)B(N{}^iPr_2)PH}$ (**160b**)			−212.6	46.2	41
$\mathrm{[Et_2NBC(H)C(H)B(NEt_2)P]_2}$ (**161a**)			−205.2	46.5	41
$\mathrm{[{}^iPr_2NBC(H)C(H)B(N{}^iPr_2)P]_2}$ (**161b**)	1.933 1.935	314.0	−195.7	48.9	41
$\mathrm{{}^iPr_2NBC(H)C(H)B(N{}^iPr_2)P({}^tBu)P({}^tBu)}$ (**162a**)	1.957	311.6	−77.4	41.5	40
$\mathrm{Me_2NBC(H)C(H)B(NMe_2)P({}^tBu)P({}^tBu)}$ (**162b**)			−92.8	40.5	40
$\mathrm{[({}^tBuP)_2(BCl)_2C_2H_4]_2}$ (**163**)	2.02 2.00	pyr pyr	19.9 14.7	4.2	39
$\mathrm{[({}^tBuP)_2(BCl)_2CH_2]_2}$ (**164**)	2.041(2) 2.036(2)	pyr pyr	2.03		39
$\mathrm{{}^iPr_2NBN({}^tBu)P(N{}^iPr_2)}$ (**167**)			−40.6	24.0	36
$\mathrm{{}^tBuNB(Cl)N({}^tBu)PCl}$ (**168a**)			160.6	25.7	36
$\mathrm{{}^tBuNB(Cl)N({}^tBu)PNEt_2}$ (**168b**)			80.0	29.9	36
$\mathrm{{}^tBuNB(Cl)N({}^tBu)PEt}$ (**168c**)			111.5	20.7	36
$\mathrm{{}^tBuNB(Cl)N({}^tBu)P{}^tBu}$ (**168d**)			128.1	23.9	36
$\mathrm{{}^tBuNB(Cl)N({}^tBu)PPh}$ (**168e**)			90.2	22.2	36
$\mathrm{{}^tBuNB(Me)N({}^tBu)PMe}$ (**169a**)			126.6	34.8	36
$\mathrm{{}^tBuNB(Cl)N({}^tBu)P{}^iPr}$ (**169b**)			119.9	21.8	36
$\mathrm{{}^tBuNB(Bu)N({}^tBu)PBu}$ (**169c**)			127.5	34.6	36
$\mathrm{{}^tBuBN({}^tBu)PCH(SiMe_3)_2}$ (**171a**)			−95	18.1	37
$\mathrm{{}^tBuBN({}^tBu)PC_5Me_5}$ (**171b**)			−56.8	20.2	37
$\mathrm{{}^tBuBN({}^tBu)PN{}^iPr_2}$ (**171c**)			−46.4	17.4	37
$\mathrm{{}^tBuNB({}^tBu)P{}^tBu}$ (**171d**)			−76.9	18.2	37
$\mathrm{{}^iPr_2NBN({}^tBu)B(N{}^iPr_2)PPh}$ (**172**)	1.956(3)	pyr		36.0	36
$\mathrm{{}^iPr_2NBN({}^tBu)Si(Me)_2PPh}$ (**173**)				32.9	36
$\mathrm{TmpBN({}^tBu)B(Tmp)P{}^tBu}$ (**175a**)			−43.4	44.1	55
$\mathrm{TmpBN({}^tBu)B({}^iPr_2N)P{}^tBu}$ (**175b**)	1.97(1)	pyr	−58.3	37.9	55
$\mathrm{TmpBN({}^tBu)P{}^iPr}$ (**177**)			−91.0	24.1	58

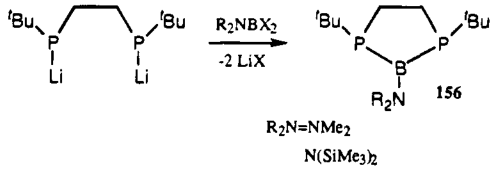
Table 9 (Continued)

compound	bond length P–B (Å)	sum of angles at P atom (deg)	$\delta^{31}P$	$\delta^{11}B$	ref
[(^{i}Pr$_2$N)BP(SiMe$_3$)N(SiMe$_3$)]$_2$ (**178**)	1.950(3)	328.4	−57.0	43.0	65
TmpBN(^{t}Bu)B(Tmp)Se (**183**)				43.8	83
TmpBN(^{t}Bu)P(^{i}Pr)(S)S (**184a**)			91.4	37.3	83
TmpBN(^{t}Bu)P(^{i}Pr)(Se)Se (**184b**)			64.1	36.8	83
[TmpBN(^{t}Bu)B(Tmp)P(^{t}Bu)Me]I (**185**)			3.9	37.7	83

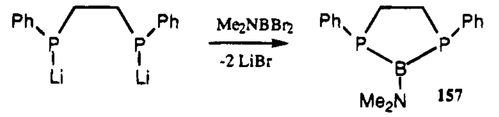
Scheme 3[83,84]



Continuing this theme, Linti[84] has prepared several additional BP_2C_2 rings by reaction of aminohaloboranes with bis(lithiophosphino)ethanes (eqs 64 and 65).



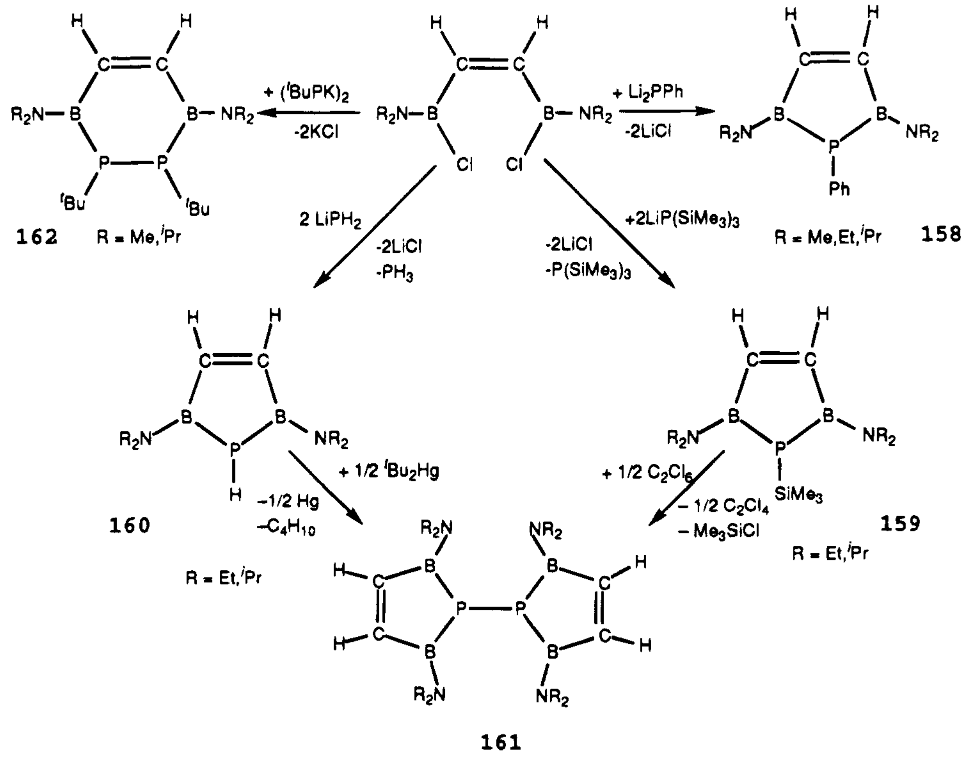
(64)[84]



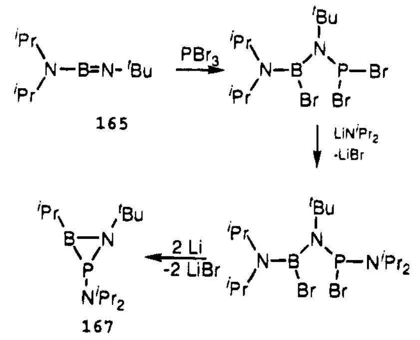
(65)[84]

Siebert and co-workers[38,40,41] reported the formation of five-membered 2,5-bis(dialkylamino)-2,5-dihydro-1*H*-1,2,5-phosphadiboroles (**158**) by double salt elimination chemistry, as shown in Scheme 4. It is interesting to note that an initial attempt to prepare the derivative ring containing a $PSiMe_3$ group by reaction of bis(dichloroboryl)ethene with $(Me_3Si)_3P$ was unsuccessful.[88] However, when the reaction was performed with $LiP(SiMe_3)_2$, the desired silylphosphane derivatives **159** were obtained. The secondary diborylphosphane derivatives **160** were formed by use of $LiPH_2$. These compounds undergo P–P coupling with formation of the diphosphanes **161**. Six-membered $B_2P_2(CH)_2$ rings **162** were produced by reaction of the diborylethenes with $(^tBuPK)_2$. Two polycyclic compounds have also been prepared by reaction of bis(dichloroboryl)ethene and bis(dichlo-

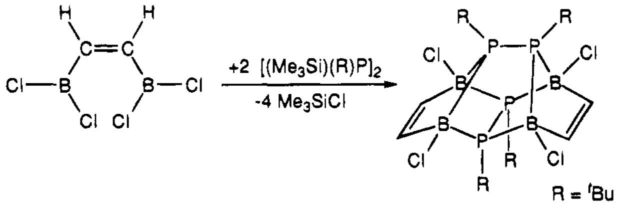
Scheme 4



Scheme 5[36]

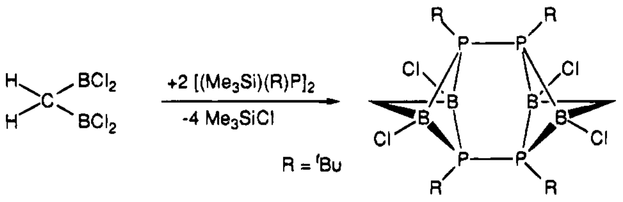


roboryl)methane with the diphosphane $[(Me_3Si)(^tBu)P]_2$.[39] The room temperature reactions proceed with Me_3SiCl elimination to give the indicated products **163** and **164** (eqs 66 and 67).



163

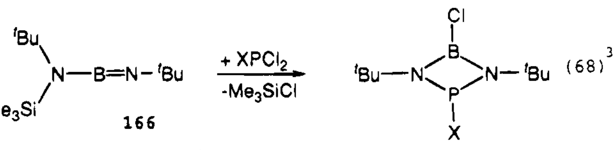
(66)[39]



164

(67)[39]

In another interesting assembly process, Paetzold and co-workers[36] utilized aminoiminoboranes $^iPr_2N{-}B{=}N^tBu$ (**165**) and $(^tBu)(Me_3Si)N{-}B{=}N(^tBu)$ (**166**) in combination with halophosphanes to prepare three-membered **167** and four-membered **168** and **169** rings (Scheme 5 and eq 68). Some limited substitution chemistry was accomplished with **168a**, and the products **169** are summarized in Scheme 6. Paetzold also examined the addition of several organosilylchlorophosphanes to the iminoborane $^tBuB{\equiv}N^tBu$ (**170**) from which three-membered rings **171** are isolated[37] (Scheme 7).

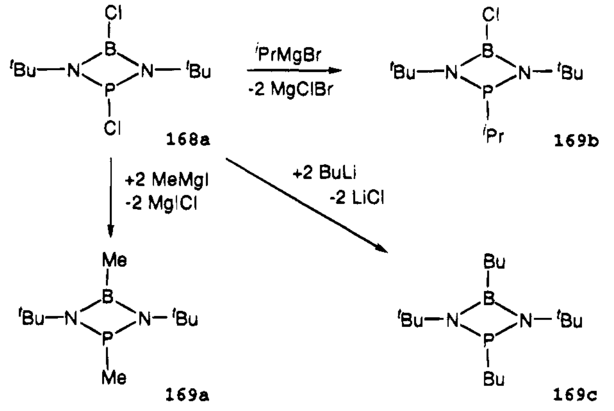


168

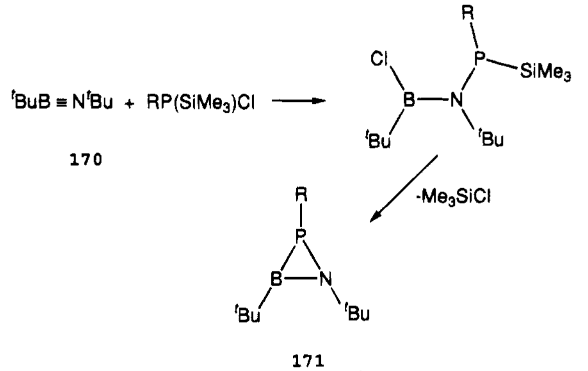
(68)[36]

The reactions of **165** with $^iPr_2NBCl_2$ and Me_2SiCl_2 also produce useful diborylamine and borylsilylamine reagents that react with Li_2PPh, resulting in BNBP **172** and BNSiP **173** four-membered ring compounds (Scheme 8).

Scheme 6[36]



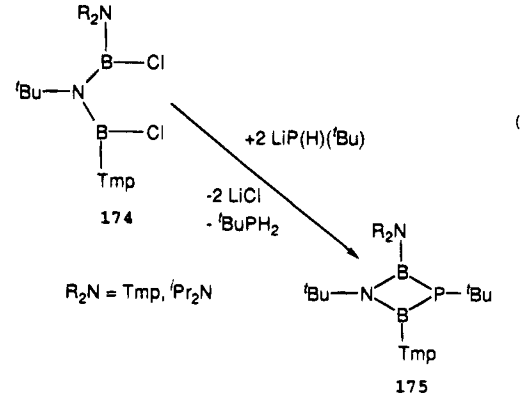
Scheme 7[37]



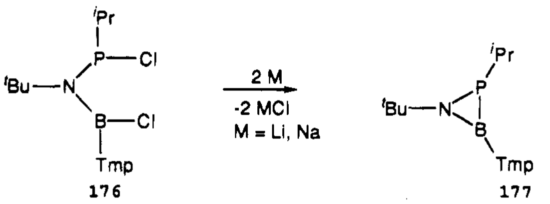
171

R = $(Me_3Si)_2CH$, Me_5C_5, $^iPr_2N$, ^{t}Bu

Several new heteroatom rings have been prepared in a related fashion from diborylamines **174**. For example, combination of $LiP(H)(^tBu)$ with **174** gives four-membered NBPB rings **175** (eq 69)[55] in good yield. The reductive coupling of the borylphosphinoamine **176** obtained from the reaction of $TmpB{\equiv}N^tBu$ and $^iPrPCl_2$ gives another example of a three-membered ring **177** (eq 70).[58] Several azido boranes are known to decompose with formation of ring compounds, and in this vein, $^iPr_2NB(N_3)PSiMe_3$ decomposes upon heating and forms the six-mem-

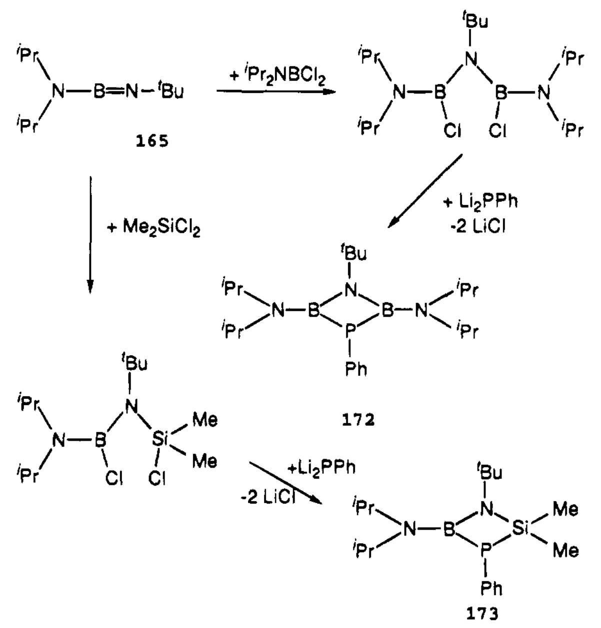


(69)[55]

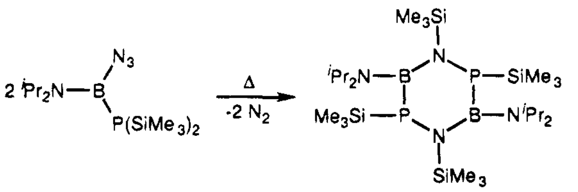


(70)[58]

Scheme 8



bered ring $[({}^{i}Pr_2NB)(NSiMe_3)(PSiMe_3)]_2$ (**178**) (eq 71).[65]



178

(71)[65]

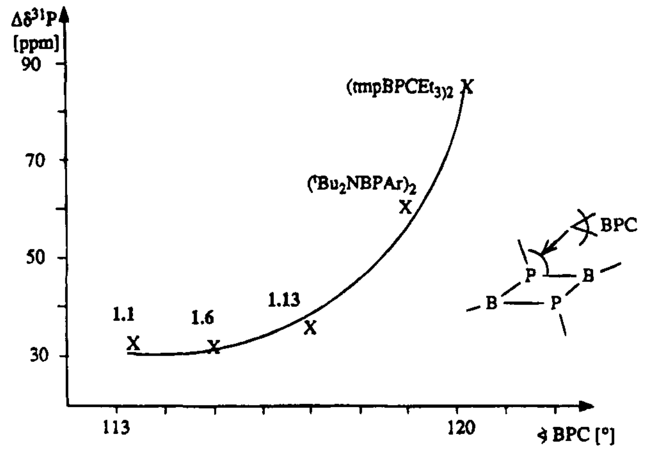


Figure 4. Relationship between ^{31}P NMR chemical shift difference ($\Delta\delta\ ^{31}P = \delta\ ^{31}P\ (R'PH_2) - \delta\ ^{31}P\ (RBPR')_2$) and exocyclic BPC bond angles (from ref 64).

B. Structural Characterization

Most of the cyclic compounds described in section III.A have been fully characterized by elemental analyses, mass spectrometry, infrared spectroscopy, and NMR spectroscopy, and some general features of the data are discussed. Most of the compounds are fairly stable to heat and electron impact ionization at 30 eV and even at 70 eV. As a result, the parent ions are usually observed with significant intensity in the mass spectra. The fragmentation processes are typically dominated by loss of the organic substituent bonded to the phosphorus atoms (e.g., Bu, Ph, Mes). Those compounds containing P–H bonds often lose PH_3 or $PH_2^{\bullet}$ in the initial ionization process. It is interesting in fact that the six-membered ring species (e.g. **122–124**) lose PH_3 and form bicyclic $P_2(R_2NB)_3^{\bullet+}$ species. The stability of these ions has been demonstrated as well by the appearance of the ions in the mass spectra of the neutral species $P_2(R_2NB)_3$ described in section IV.

The infrared spectra for the compounds described in this section are rich with bands, so only a few features are particularly noteworthy and useful for characterization purposes. In particular, those compounds containing a P–H group normally have a medium to weak band in the region 2400–2200 cm^{-1} that can be assigned to a P–H stretching mode. Further, in cases where the members of a set of compounds are very similar except for minor steric or electronic shifts due to substituent group variations, the differences in ν_{PH} can be used to deduce small shifts in the P atom hybridization. In many of the compounds, the B–N stretching mode(s) can also often be assigned in the region 1500–1250 cm^{-1}.

As found with the acyclic compounds described in section II, multinuclear NMR data for the cyclic phosphinoboranes are especially useful. The ^{1}H and $^{13}C\{^{1}H\}$ NMR data typically confirm the structural integrity and identity of organic substituent groups, while $^{11}B\{^{1}H\}$ and $^{31}P\{^{1}H\}$ NMR data provide information on coordination numbers and structural/substituent group variations. For example, the ^{11}B NMR resonances for the cyclic species (Tables 6–9) typically fall in the chemical shift region associated with three-coordinate boron (δ 100–20),[86] and only a few shifts appear with $\delta < 30$. The line widths for these resonances are generally broad ($h_{1/2} > 100$ Hz) and resolved B–P coupling is unusual. The resonance positions in the ^{31}P NMR spectra at constant coordination number are most strongly affected by the electronic nature of the substituent groups on phosphorus. Electronic features appear to be so dominant that they often mask trends that might be used to unambiguously deduce ring size in response to bond angle variations. Nonetheless, Linti[64] has noted that ^{31}P chemical shifts in some 1,3,2,4-diphosphadiboretanes correlate with square and rhomboidal B_2P_2 ring structures. In a family of 1,3-organyl-2,4-amino-1,3,2,4-diphosphadiboretanes, it is found that $\delta\ ^{31}P$ is more downfield (deshielded) in the square rings than the rhomboids. Some representative data are summarized in Figure 4. This plot correlates the differences in ^{31}P chemical shift between parent phosphines RPH_2 and the diphosphadiboretanes, $\Delta\delta\ ^{31}P$, with the exocyclic B–P–C bond angle. Qualitatively, this suggests that an increasing deviation from the ideal phosphane bond angle (PH_3, H–P–H 93.5°) leads to larger deshielding. A similar trend has been noted for polyphosphines.[89,90]

Power and co-workers[14,18,19] have noted that the ^{31}P chemical shifts in the six-membered boraphosphabenzenes **117–121** lie approximately 70 ppm downfield of the shifts for related four-membered ring compounds. This is not totally unexpected since the latter compounds contain pyramidal phosphorus atoms, while the former have planar phosphorus atom environments. Further, the six-membered rings show upfield shifts in the ^{11}B NMR spectra. It is also found that the ^{1}H NMR shifts for *o*-Me groups on mesityl substituents are 0.4–0.7 ppm shifted from *p*-Me groups. These data are consistent with significant delocalization of electron density and ring current effects in the B_3P_3 planar rings.

As noted below, the amino B-substituted four- and six-membered rings contain pyramidal phosphorus atom environments. As a result, it is possible that *cis* and *trans* geometrical isomers (four-membered rings) and idealized chair, boat, and twist geometrical isomers (six-membered rings) may exist in solution. Surprisingly, there have been few reports of dynamic isomer interconversion processes.

The molecular structures of several of the cyclic compounds (Tables 6–9) have been determined by single-crystal X-ray diffraction analysis. Some general features of the structures are summarized, and some structures that have not yet appeared in easily accessible literature are presented.

As mentioned briefly above, smaller organic substituents on ring species $(RBPR)_n$ favor the trimeric, six-membered ring composition, while larger organic substituents favor the dimeric, four-membered ring composition.[14,16] A similar steric trend is found for amino-substituted rings $(R_2NBPR')_{2,3}$.[65] The organo-substituted, six-membered rings are generally planar, and they have relatively short B–P bond distances, ~1.84 Å,[11,14] while amino-substituted, six-membered rings are nonplanar with cyclohexane-like chair or twist conformations and relatively long B–P bond distances, >1.9 Å (e.g., $[(Me_3Si)_2NBPH]_3$ (**125**) twisted chair, average B–P 1.928(10) Å). The H atoms reside in the equatorial positions. The organo-substituted, six-membered rings are proposed to have extensive delocalization in a fashion related to borazine rings, while the amino-substituted, six-membered rings have little or no ring delocalization since the boron atom's electron deficiency is satisfied by the *exo* amino groups. It is interesting to point out that the six-membered heteroatom ring $[^iPr_2NBP(SiMe_3)N(SiMe_3)]_2$ (**178**) also has a nonplanar, cyclohexane-like structure with a boat conformation in which the ring N atoms occupy the prow positions.[65] The boron atoms have a planar geometry, while the phosphorus atoms have a pyramidal geometry. The B–P bond distance is long, 1.950(3) Å, and the *exo* B–N^{i}Pr$_2$ bond distance (1.407(4) Å) is shorter than the *endo* B–N(SiMe$_3$) bond distance (1.475(3) Å).

In general, the four-membered ring compounds B_2P_2 and $B_nP_m(EX)$ are planar with a trigonal planar boron atom geometry and pyramidal phosphorus atom geometry. In all cases, the phosphorus atom *exo* substituents have a *trans* orientation. Those compounds containing an N atom in the ring or in an amino substituent are also planar. The B–P bond distances in all of these compounds are relatively long (1.896–2.041 Å), and they are considered to be B–P single bonds. In molecules with terminal B–NR$_2$ groups, the B–N bond distances are generally short, suggesting a significant degree of B–N π overlap at the expensve of potential B–P π overlap.

The molecular structures of both $(^iPr_2NBPH)_2$ (**94**) and $(^iPr_2NBPH)_3$ (**122**) have recently been determined,[87] and their structural features illustrate a number of the points summarized above. Views of the molecules are shown in Figures 5 and 6. The four-membered ring **94** is centrosymmetric with trigonal planar $^iPr_2NB$ fragments and pyramidal phosphorus atoms. The average B–P bond distance, 1.931(3) Å, is in the single bond range, while the B–N bond distance, 1.377(3) Å, is quite short and is consistent with significant B–N π overlap. The six-membered ring **122** has a twist cyclohexane structure with the H atoms in equatorial sites. The average B–P bond distance, 1.933(7) Å, is identical to the average distance in **94**. As expected, however, the internal angles at the P and B atoms are strongly different: **94** B–P–B 84.3°, P–B–P 95.7°; **122** B–P–B(avg) 105.9°, P–B–P(avg) 111.5°.

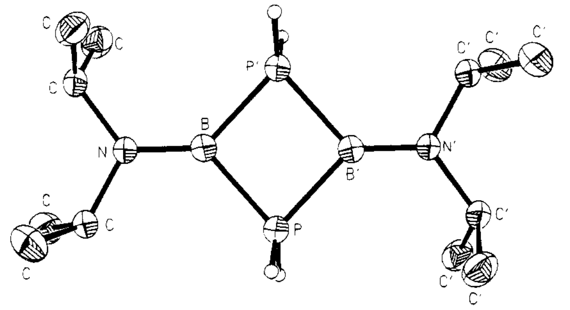


Figure 5. Molecular structure of $[^iPr_2NBPH]_2$ (**94**).

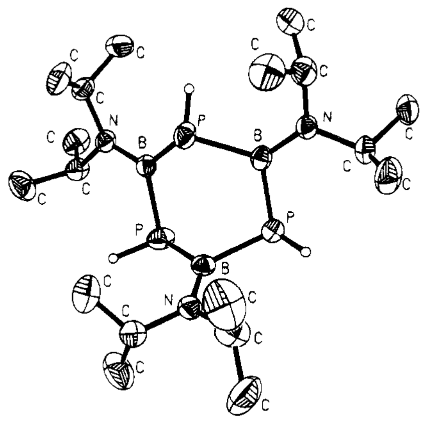


Figure 6. Molecular structure of $[^iPr_2NBPH]_3$ (**122**).

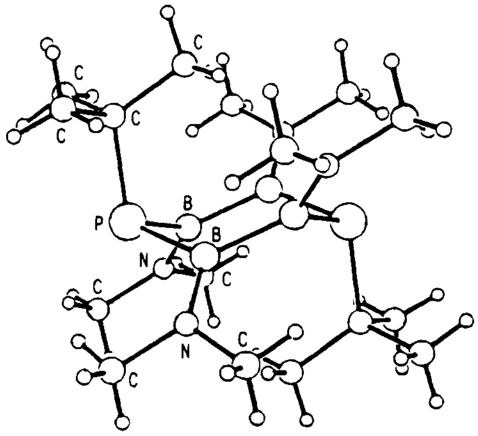


Figure 7. Molecular structure of $(Me_2NB)_4(^tBuP)_2$ (**144**).

The molecular structure of the six-membered B_4P_2 ring **144** has recently been determined,[83] and a view of the molecule is shown in Figure 7. The ring has a chair conformation with the ^{t}Bu groups oriented *trans*

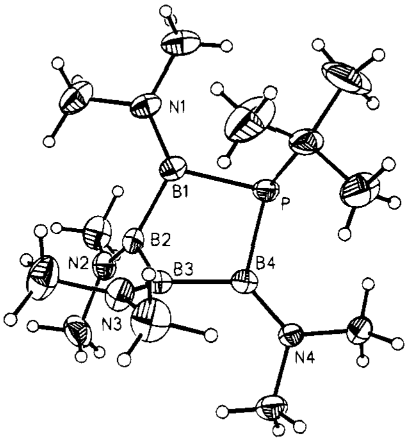


Figure 8. Molecular structure of (Me$_2$NB)$_4$(^{t}BuP) (**146**).

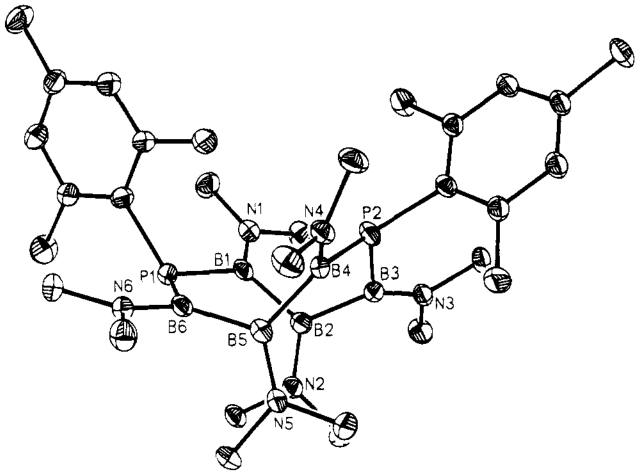


Figure 9. Molecular structure of (Me$_2$NB)$_6$(MesP)$_2$ (**147**).

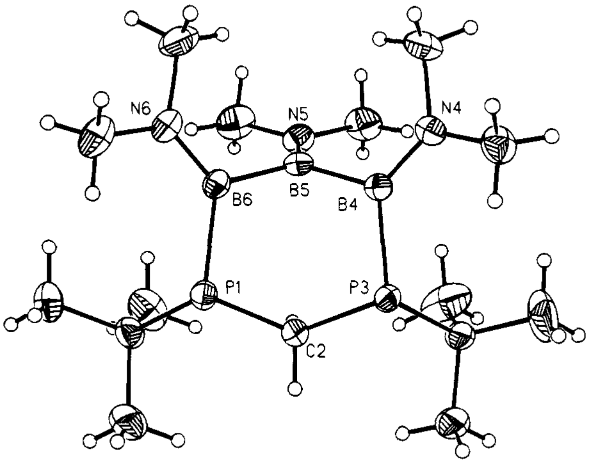


Figure 10. Molecular structure of (Me$_2$NB)$_3$(^{t}BuP)$_2$CH$_2$ (**154**).

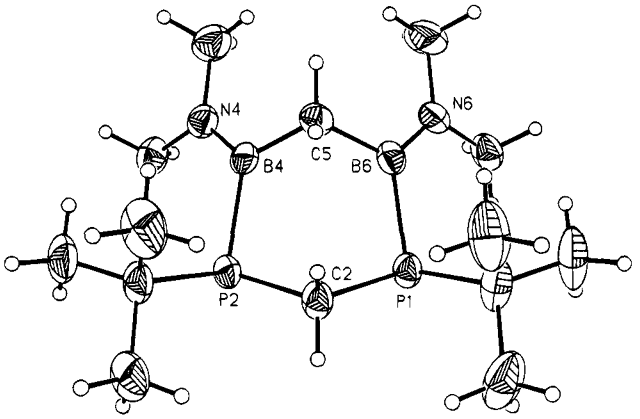


Figure 11. Molecular structure of (^{i}Pr$_2$NB)$_2$(^{t}BuP)$_2$(CH$_2$)$_2$ (**152**).

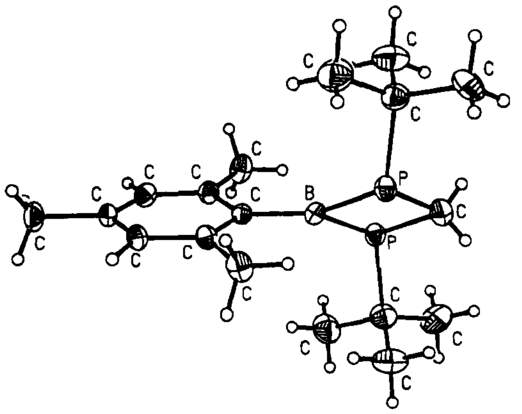


Figure 12. Molecular structure of (MesB)(^{t}BuP)$_2$CH$_2$ (**150**).

to each other. The B–P bond distances are 1.99 Å and 1.96 Å, and the B–B bond distance is 1.697 Å.

The structure of the only five-membered B$_4$P ring (Me$_2$NB)$_4$^{t}BuP (**146**) has been determined,[83] and a view of the molecule appears in Figure 8. This molecule has a twisted envelope configuration, with the B(2) and B(3) atoms occupying positions below and above the plane formed by B(1), B(4), and P. The B–P distances, 1.978(3) and 1.958(3) Å, are clearly in the single-bond range. The B(3)–B(4) bond distance, 1.678(4) Å, is shorter than the other two B–B bond distances, 1.704(5) Å (avg). The molecular structure of the only reported member of the eight-membered ring family (Me$_2$NB)$_6$(MesP)$_2$ (**147**) is available.[84] A view of the molecule is shown in Figure 9. The ring has a distorted tub shape with planar boron atoms and pyramidal phosphorus atoms. The average B–P bond distance, 1.920 Å, also falls in the single-bond range.

The molecular structures of two six-membered heteroatom rings have recently been solved, and views of (Me$_2$NB)$_3$(^{t}BuP)$_2$CH$_2$ (**154**) and (^{i}Pr$_2$NB)$_2$(^{t}BuP)$_2$(CH$_2$)$_2$ (**152**) are shown in Figures 10 and 11, respectively. Compound **154** adopts a boat conformation, and the ^{t}Bu groups are *cis* to each other and *trans* with relation to the nearest NMe$_2$ groups. The average B–P bond distance, 1.968(10) Å, is relatively long compared to the distances in four-membered rings. The molecular structure of **152** displays a twist conformation with the ^{t}Bu groups approximately *trans* to each other. The average B–P bond distance, 1.990(5) Å, is even longer. In contrast, the molecular structure of the four-membered heteroatom ring (MesB)(^{t}BuP)$_2$CH$_2$ (**150**) has been obtained,[84] and a view is shown in Figure 12. The mesityl ring lies in the plane of the BP$_2$C plane, and the ^{t}Bu groups are *trans* to each other. The average B–P bond distance is comparatively short, 1.884(6) Å.

Finally, the molecular structure of only one three-membered ring, (^{t}BuP)$_2$BNEt$_2$ (**130**), has been examined,[29] and it also displays a normal B–P single bond distance, 1.892(2) Å, with pyramidal phosphorus centers and ^{t}Bu groups in *trans* positions.

C. Reaction Chemistry

The cyclic compounds described above have several sites of reactivity including the phosphorus lone pair, the B−P bond and B-substituent and P-substituent bonds. Although most of the cyclic compounds have been known for only a short time some examples of reactivity in these molecules have been revealed.

1. Behavior toward Bases

The boron atoms in many of these cyclic compounds appear to be relatively electron saturated as a result of π overlap with either phosphorus atoms in the ring or nitrogen atoms in *exo* substituent groups or in the ring. As a result, they show little residual boron-centered Lewis acidity. Those compounds containing P−H bonds, on the other hand, react readily with strong bases (eq 53). The resulting phosphido anions are useful for the preparation of P-substituted rings (eq 54) and bicyclic species (section IV). The molecular structures of two lithium salts of diphosphadiboretanes have been determined, and the association of the Li cation with the anions is quite different. In the case of TmpBP(H)(TmpB)PLi·TMEDA (Figure 13),[84] the molecule is monomeric, and the Li ion is positioned over the top of the B_2P_2 ring. This compound is therefore a member of the bicyclic family B_2P_2E discussed in section IV. Surprisingly, the P(1)−Li distance associated with the P−H unit, 2.521(4) Å, is slightly shorter than the P(2)−Li distance corresponding to the phosphide center, 2.559(4) Å. The four-membered B_2P_2 ring is no longer planar as in the parent compound **95**, but the average B−P bond distances are identical: 1.923(3) Å vs 1.924(4) Å in **95**. As expected, the average B−P distance associated with the phosphide anion P(2), 1.919(3) Å, is shorter than the average distance associated with P(1), 1.928(3) Å. This may indicate the source of the unexpected P−Li distances. The molecular structure of [^{i}Pr$_2$NBP(H)(^{i}Pr$_2$NB)PLi·DME] is dimeric (Figure 14), and its structure has been discussed in detail.[65] Briefly, the two nonplanar B_2P_2 rings are joined through an asymmetric planar (rhomboidal) Li_2P_2 ring. The two B_2P_2 rings are approximately perpendicular to the Li_2P_2 ring. In this case as well, the B−P bond distances associated with the phosphide P atoms are significantly shorter than those involving the phosphane P atom: 1.901(6) Å vs 1.950(6) Å.

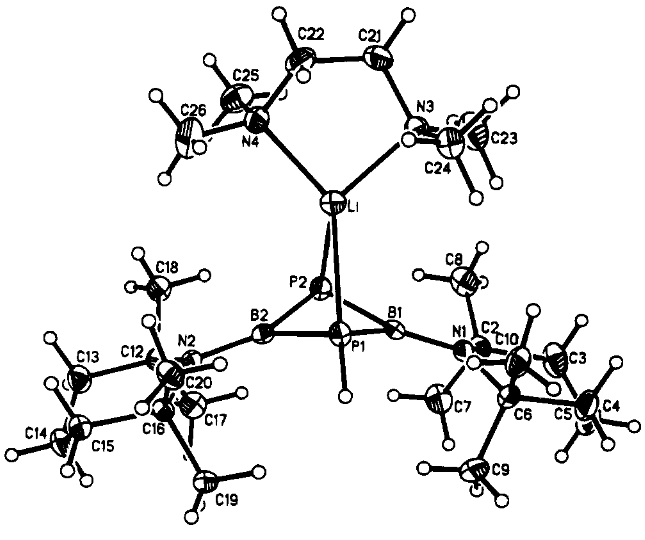


Figure 13. Molecular structure of TmpBP(H)(TmpB)PLi·TMEDA.

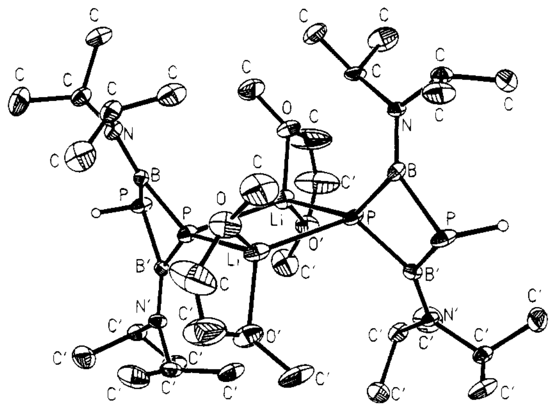
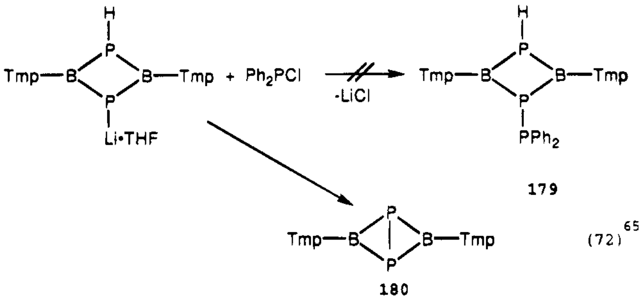


Figure 14. Molecular structure of [^{i}Pr$_2$NBP(H)(^{i}Pr$_2$NB)PLi·DME]$_2$.

Returning to the chemistry of the anions, it is interesting, however, that addition of Ph_2PCl to TmpBP(H)B(Tmp)PLi·(THF) does not lead to a P-phosphanated product **179** (eq 72). Instead, the bicyclic cage compound $(TmpBP)_2$ (**180**) is obtained.[65] Additional examples of these four-atom bicyclic cages are described in section IV. Addition of a strong base such as alkyl lithium reagents to cyclic phosphinoboranes without a P−H group typically leads either to no reaction or to ring opening with alkylation of the boron center(s) (eq 73).[40]



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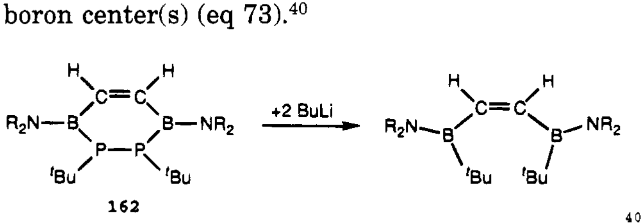
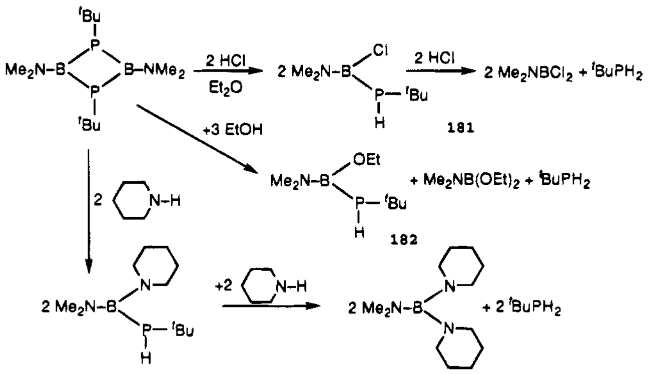


(73)[40]

2. Behavior toward Acids

The combination of reagents containing an acidic proton with a cyclic phosphinoborane generally results in addition of HX across the B−P bond. Several examples[64] of this chemistry are summarized in Scheme 9. Attempts to add Lewis acids such as BH_3

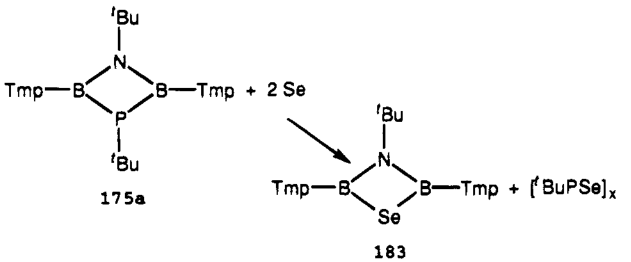
Scheme 9[64]



or BCl_3 to 1,3,2,4-diphosphadiboretanes have not yet produced stable acid−base adducts. This is interesting since most of the cyclic ring compounds readily form stable complexes with metal carbonyl fragments.

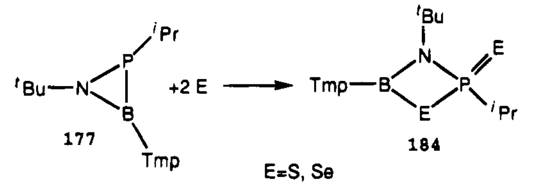
3. Redox and Nucleophilic Displacement Reactions

The redox chemistry of cyclic phosphinoboranes has also been examined in a cursory way. For example, combination of **175a** with Se leads to expulsion of the



(74)[55]

^{t}BuP group (eq 74).[55] The addition of S and Se to **177** leads to ring opening as well, but the phosphorus group is retained, and the resulting expanded ring contains S or Se (eq 75).[58] The addition of CH_3I to



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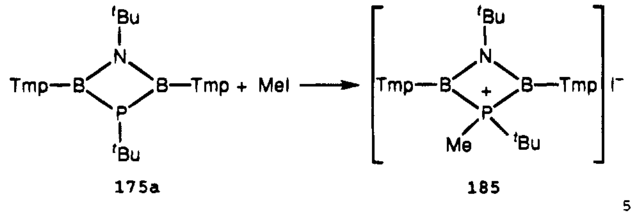

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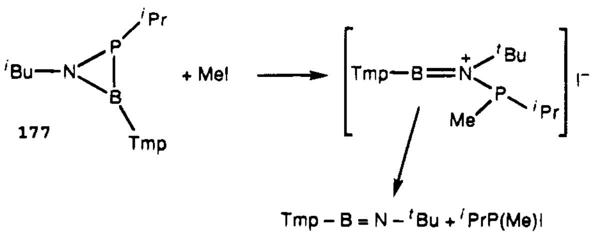


(77)[58]

175a and **177** leads to formation of phosphonium salts (eqs 76 and 77).[55,58]

It was mentioned above that TmpBP(H)B(Tmp)PLi·THF combines with Ph_2PCl in an unexpected fashion to produce a novel bicyclobutane analog $(TmpBP)_2$ (**180**).[50] It has also been observed that several 1,3,2,4-diphosphadiboretanes are subject to intramolecular reductive P−P coupling when irradiated with UV light or combined with AIBN.[50] This chemistry is discussed further in section IV.A.1.

4. Behavior as Ligands

As noted above, the coordination chemistry of many cyclic phosphinoboranes has been explored with metal carbonyl fragments. Some illustrative examples are shown in eqs 78−86, and most of the characterized complexes are summarized in Table 10.

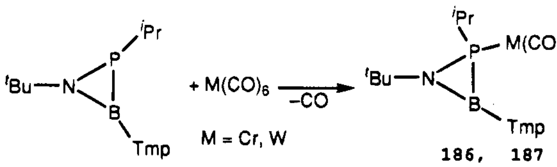
All of the complexes contain direct metal−phosphorus bonding, and the M−P bond distances fall in the normal ranges established for metal carbonyl−phosphane complexes. In general, the 1,3,2,4-diphosphadiboretanes with P−H units and amino substituents on boron form *exo* monometallic complexes,[55,59,63,64] and this is clearly evidenced by ^{31}P NMR spectra that show a resonance for a coordinated phosphane and a free phosphane. Molecular structure determinations also confirm this structure assignment. Presumably, the Lewis basicity of the second P−H center is reduced by the first metal binding interaction. The six-membered ring $[(Me_3Si)_2NBPH]_3$ also forms only a monometallic complex and the $Cr(CO)_5$ fragment is bonded in an *exo* position. So far, in only one instance (**190**) has a bimetallic *exo* complex been isolated and characterized, and this compound displays a *trans* arrangement of its two $Cr(CO)_5$ fragments.[66] Whether or not other P-alkyl-substituted B_2P_2 rings reveal bimetallic coordination remains to be demonstrated.

Novel coordination chemistry of the B−P compounds has been recently revealed with (MesBP^{t}Bu)$_2$ (**84**) and $(MesBPPh)_3$ (**119**). Combination of **84** with $Cr(CO)_5$·THF gives **192** as a yellow crystalline solid and with $Fe_2(CO)_9$ a red, light-sensitive compound **193** is initially obtained that, upon irradiation, readily loses CO and forms **194**.[68] NMR data suggested the formation of highly symmetrical *nido* structures for **192** and **194**, and this was confirmed by X-ray diffraction analyses. It is found that the B_2P_2 rings in the clusters are slightly folded, whereas the ring in **84** is strictly planar, and the B−P bond distances are more irregular: **192**, 1.911(7) and 1.864(6) Å; **194**, 1.94−1.89 Å. The reaction of planar heteroaromatic **119** with $Cr(CO)_3(CH_3CN)_3$ gives the novel compound **195**. The crystal structure determination for this compound[88] shows that the B_3P_3 ring remains nearly planar, and the $Cr(CO)_5$ fragment is positioned almost exactly over the centroid of the ring. Coordination again results in no significant change in the average B−P bond lengths in the ring, although as with **194**, the range of B−P distances is greater than in the free ligand. This *nido*

Table 10. Metal Carbonyl Complexes of Cyclic Phosphinoboranes

compound	bond length B−P (Å)	ν(CO) (cm^1)	δ^{31}P	δ^{11}B	ref
$\mathrm{TmpBN(^tBu)P(^iPr)[Cr(CO)_5]}$ (**186**)			−220	21.7	58
$\mathrm{TmpBN(^tBu)P(^iPr)[W(CO)_5]}$ (**187**)			−67.2	25.0	58
$\mathrm{TmpBN(^tBu)B(Tmp)P(^tBu)[W(CO)_5]}$			−21.4	42.2	55
$\mathrm{^iPr_2NBN(^iPr)C(Me)_2P(TmpB(H))[Fe(CO)_4]}$ (**188**)	1.965(8) 1.964(8)	2037 1962 1927	−3.4	38.4 30.5	63
$\mathrm{Me_2NBP(^tBu)B(NMe_2)P(^tBu)[Cr(CO)_5]}$ (**219**)		2040 1987 1940	−42.0 −34.5	45.9	59, 64
$\mathrm{Et_2NBP(^tBu)B(NEt_2)P(^tBu)[Cr(CO)_5]}$ (**189**)		2049 1928 1898	−41.1 −38.1	44.5	64
$\mathrm{Et_2NBP(^tBu)B(NEt_2)P(^tBu)[Cr(CO)_5]_2}$ (**190**)	1.975(2) 1.972(2)		−27.2	43.7	64
$\mathrm{^iPr_2NBP(CEt_3)B(N^iPr_2)P(CEt_3)[Cr(CO)_5]}$	1.997(3) 1.980(3) 1.881(3) 1.885(3)	2048 1925 1900	−58.7 −45.2	46.4	64
$\mathrm{TmpBP(Trip)B(Tmp)P(Trip)[Cr(CO)_5]}$					64
$\mathrm{TmpBP(H)B(Tmp)P(H)[Cr(CO)_5]}$	1.963(5) 1.967(5) 1.938(5) 1.939(5)	2057 1974 1935	−108.2 −91.0	46.4	65
$\mathrm{[(Me_3Si)_2NBPH]_3[Cr(CO)_5]}$ (**191**)	1.965(8) 1.983(8) 1.920(8) 1.906(8) 1.903(8) 1.953(8)	2060 1981 1940 1923	−91.0 −69.3	62.0	65
$\mathrm{[MesBP(^tBu)]_2[Cr(CO)_4]}$ (**192**)	1.864(6) 1.911(7)	2000 1991 1918 1899	−39.8	29.7	68
$\mathrm{[MesBP(^tBu)]_2[Fe(CO)_4]}$ (**193**)		2022 1970 1958	14.6 49.0	8.5	68
$\mathrm{[MesBP(^tBu)]_2[Fe(CO)_3]}$ (**194**)	1.94(1) 1.910(8) 1.888(8) 1.872(10)	2003 1946 1934	53.9	7.3	68
$\mathrm{[MesBP(^tBu)]_3[Cr(CO)_3]}$ (**195**)	1.840(7) 1.865(7) 1.833(7) 1.844(6) 1.865(7) 1.842(6)	1931 1863	20.3	20.9	88
$\mathrm{Me_2NBC(H)C(H)B(NMe_2)P(^tBu)P(^tBu)[Cr(CO)_4]}$ (**196a**)		2011 1942 1902	−60.7 −28.1	−8.5	40
$\mathrm{^iPr_2NBC(H)C(H)B(N^iPr_2)P(^tBu)P(^tBu)[Cr(CO)_4]}$ (**196b**)		2013 1942 1924 1905	−46.8 −27.7	−7.5	40
$\mathrm{[Et_2NBC(H)C(H)B(NEt_2)P]_2[Cr(CO)_5]_2}$ (**197**)	1.965(5) 1.983(6) 1.968(5) 1.985(5)	2059 1977 1937	−162.7	45.9	41
$\mathrm{[Et_2NBC(H)C(H)B(NEt_2)P]_2[Fe(CO)_3]_2}$ (**198**)	1.94(avg)	2031 2022 1961 1952	−111.8	30.8	41

structure is strongly reminiscent of the (η^6-hexamethylborazine)$\mathrm{Cr(CO)_3}$ complex in which the borazine ring is puckered and the Cr−CO vectors align over the borazine N atoms. Attempts are in progress to expand this chemistry and to understand the detailed features of the bonding.



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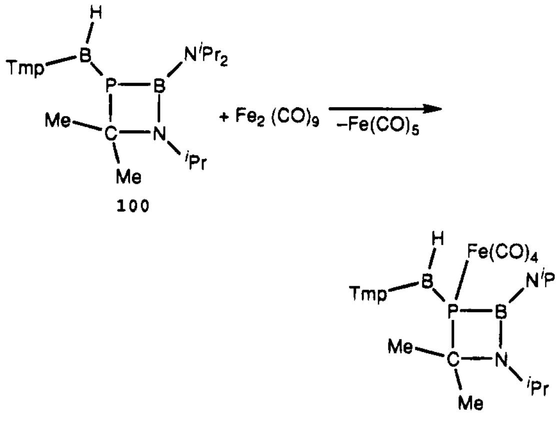

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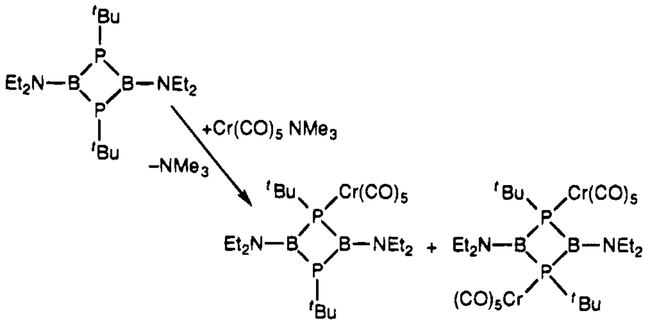

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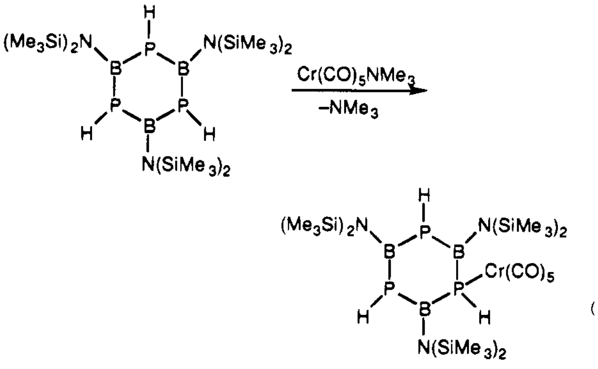

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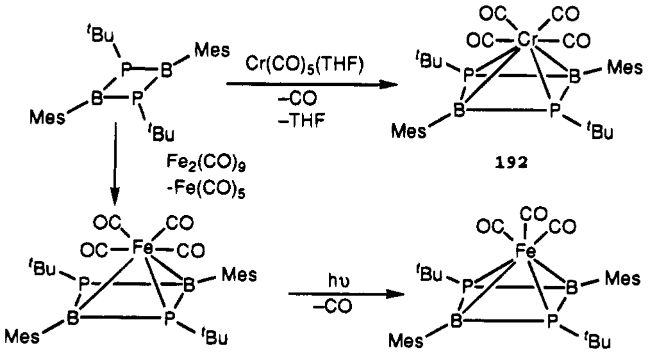

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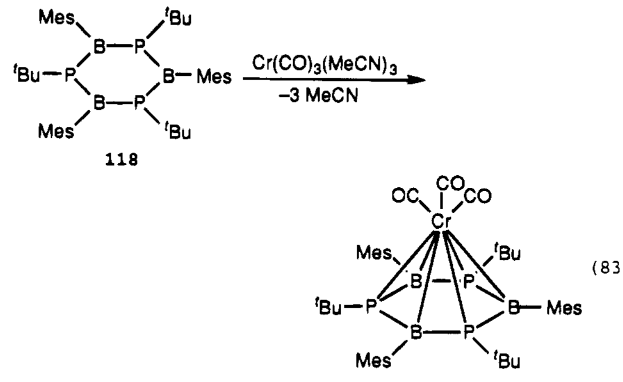

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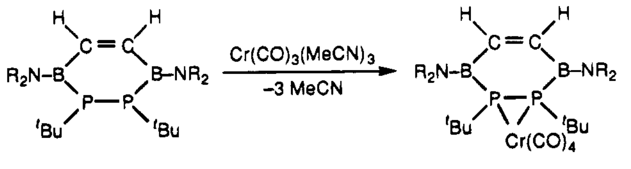
(83)[86]



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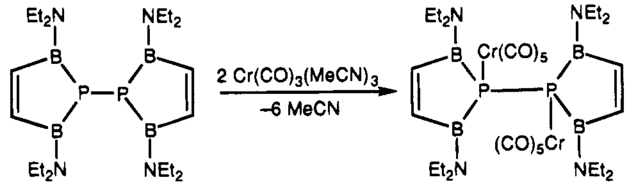
196 a,b

(84)[40]



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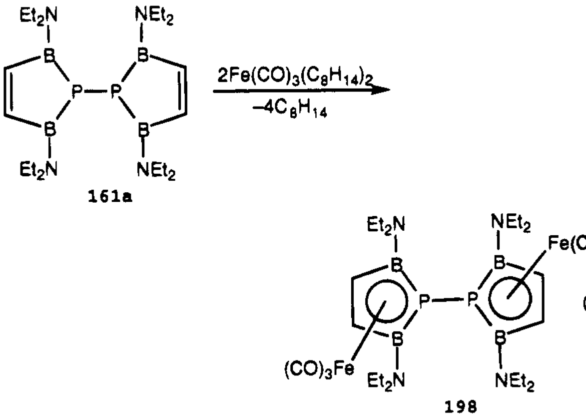

161a

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(86)[41]

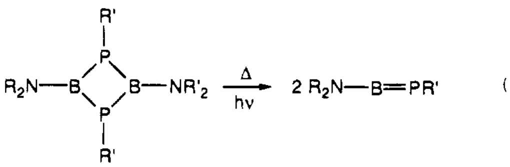
IV. Bicyclic Systems

On the basis of the rich diversity of organic bicyclic compounds and boron hydride and carborane cage compounds, it is reasonable to expect parallel boron–phosphorus polycyclic cage structures to exist. However, prior to 1987, no such compounds were known. New results now indicate that this absence was not a consequence of inherent cage instabilities, but instead a lack of efforts to prepare and isolate these compounds.

A. Preparation

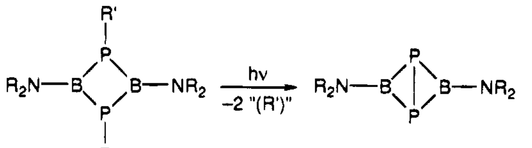
1. The B_2P_2 Bicyclo[1.1.0]butane System

It was noted in sections II and III that sterically congested diphosphadiboretanes have been prepared in several groups as potential sources for monomeric boranylidenephosphanes (eqs 17 and 87). In the



(87)

course of these studies, Nöth and co-workers[50] found, however, that an additional reaction pathway exists when a few 1,3,2,4-diphosphadiboretanes are photolyzed: reductive coupling of the phosphorus atoms that leads to formation of 1,3,2,4-diphosphadiborabicyclo[1.1.0]butanes (**199**). However, it is important to note that this reaction is not general. So far, the reductive P–P coupling (eq 88) is displayed by only four diphosphadiboretanes: (TmpBPCEt$_3$)$_2$, (TmpBPH)$_2$, (TmpBP^{t}Bu)$_2$, and (^{t}Bu$_2$NBPCEt$_3$)$_2$. The respective bicycles are also formed under free radical (AIBN) initiation. Studies of these compounds continue in an effort to better understand the factors controlling bicycle formation.



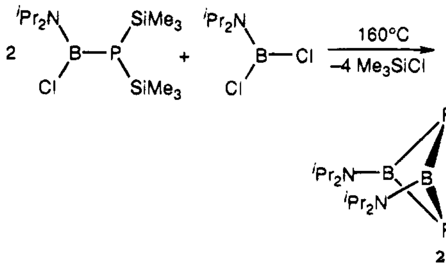
(88)[50]

199

R$_2$N/R: Tmp/CEt$_3$;Tmp/Trip; Tmp/^{t}Bu; Tmp/H; ^{t}Bu$_2$N/CEt$_3$

2. The B_3P_2, B_2P_2E, and $B_2P_2E_2$ Systems

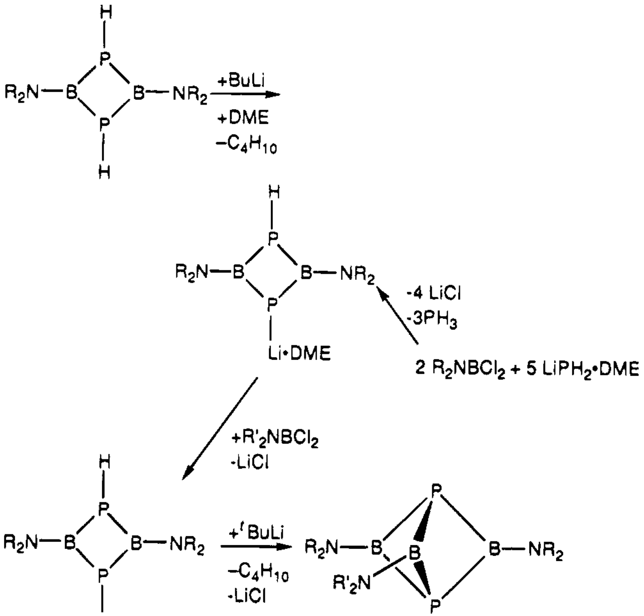
The first member of this family of compounds, (^{i}Pr$_2$NB)$_3$P$_2$ (**200**), was reported[54] in 1987 from a 2:1 reaction of ^{i}Pr$_2$NB(Cl)P(SiMe$_3$)$_2$ and ^{i}Pr$_2$NBCl$_2$ at 160 °C (eq 89). Although **200** was formed in good yield, relative derivatives were not obtained from similar reactions of R$_2$NB(Cl)P(SiMe$_3$)$_2$ and R'$_2$NBCl$_2$. Apparently, the P–SiMe$_3$ bonds are not sufficiently labile at modest reaction temperatures to encourage the facile elimination of Me$_3$SiCl. In order to circumvent this problem, Nöth and Paine chose to develop a stepwise assembly process for the general synthesis of these compounds.[62] That chemistry is summarized in Scheme 10. In each case, the P-borylated diphosphadiboretane was isolated in good yield (see section III.C.1), and dehydrohalogenation was spontaneous or was promoted with ^{t}BuLi. This chemistry allows formation of symmetrically substituted derivatives, (^{i}Pr$_2$NB)$_3$P$_2$ (**200**) and (TmpB)$_3$P$_2$ (**201**), and asymmetrically substituted derivatives, (R$_2$NB)$_2$(R'$_2$NB)P$_2$ (**202–205**) (Table 11).



(89)[54]

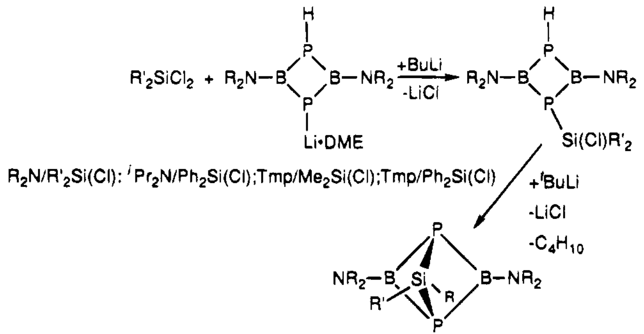
200

Scheme 10



202 - 205

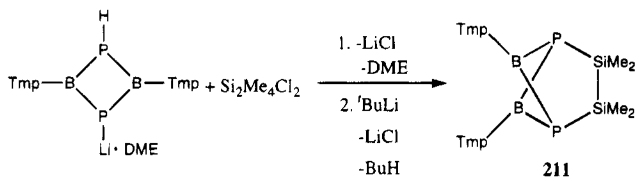
Scheme 11



R$_2$N/R'$_2$Si(Cl): ^{i}Pr$_2$N/Ph$_2$Si(Cl);Tmp/Me$_2$Si(Cl);Tmp/Ph$_2$Si(Cl)

206-208

Scheme 12



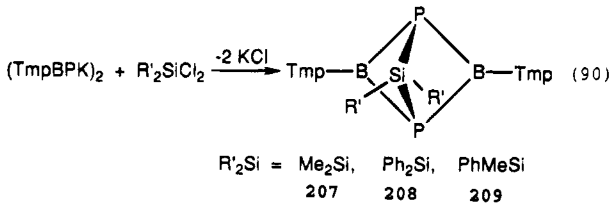
211

Extending this chemistry, the reactions of R$_2$NBP(H)(R$_2$N)BPLi·DME with R$_2$SiCl$_2$ were examined, and it was found that P-silylated diphosphadiboretanes formed.[67] These species also undergo dehydrohalogenation in the presence of ^{t}BuLi, and the new cage compounds (R$_2$NB)$_2$(R'$_2$Si)P$_2$ (**206–208**)

Table 11. Structural and NMR Data for Bicyclic Compounds

compound	bond length P−B (Å)	sum of angles at P (deg)	δ^{31}P	δ^{11}B	ref
$(TmpBP)_2$ (**199a**)	1.904(2)(avg)	109.9	−290.1	45.1	50
$(^tBu_2NBP)_2$ (**199b**)			−293.4	44.8	50
$(^iPr_2NB)_3P_2$ (**200**)	1.969(8)(avg)		−13.0	40.5	54
$(^iPr_2NB)_2(TmpB)P_2$ (**202**)			10.1	43.7 39.7	62
$(^iPr_2NB)_2[(Me_3Si)_2NB]P_2$ (**203**)	1.948(7)(avg)	203.6	23.5	53.0 39.2	62
$(TmpB)_2(^iPr_2NB)P_2$ (**204**)			32.0	42.8 38.6	62
$(TmpB)_2[(Me_3Si)_2NB]P_2$ (**205**)			69.2	51.1 41.9	62
$(TmpB)_3P_2$ (**201**)	1.958(6)(avg)	214.2	54.3	42.7	62
$(^iPr_2NB)_2(Ph_2Si)P_2$ (**206**)	1.973(6)(avg)	212.6	−18.4	45.4	67
$(TmpB)_2(Me_2Si)P_2$ (**207**)			31.3	49.2	67
$(TmpB)_2(Ph_2Si)P_2$ (**208**)	1.992(7)(avg)	216.8	32.2	48.2	67
$(TmpB)_2(PhMeSi)P_2$ (**209**)			30.6	48.5	67
$(TmpB)_2(MeSiSiMe_2)P_2$ (**211**)	1.978(5)(avg)	263.9	−13.4	57.2	67
$(^iPr_2NB)_2(MeSiSiMe_2)P_2$ (**213**)	1.929(4)(avg)	256.3	−84.9	51.7	67
$(TmpB)_2(Ph_2Ge)P_2$ (**214**)	1.97(1)(avg)		49.8	47.3	91
$[(^iPr_2NB)_2P_2Si]_2(^iPr_2NBP)_2$ (**217**)			9.0 −59.0	50.8 42.8	92
$[(^iPr_2NB)_2P_2]_2Si$ (**216a**)	1.976(2)(avg)		−6.5	45.7	69
$[(TmpB)_2P_2]_2Si$ (**216b**)	1.97(2)(avg)		38.9	48.6	69

were obtained. This chemistry is summarized in Scheme 11. A one-step reaction (eq 90) has also been



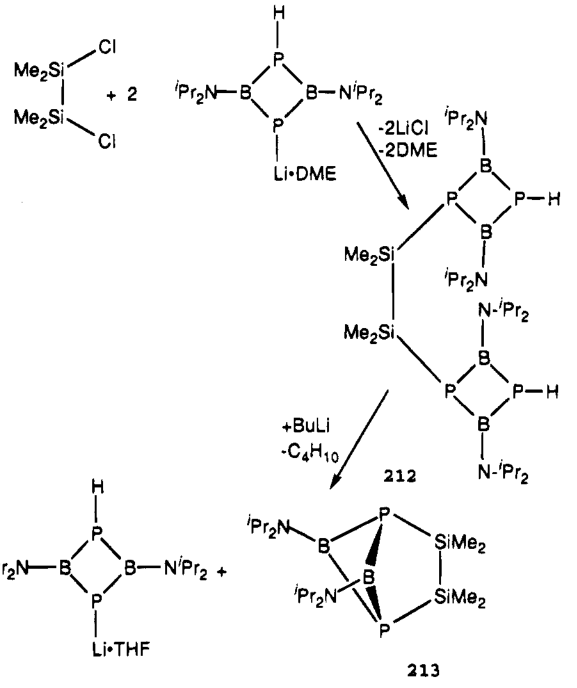
used to make several of these compounds; however, in some cases, the bicyclobutane derivative **199** is formed instead of the desired cage molecules.

The reaction of TmpBP(H)B(Tmp)PLi·DME with the disilane $Me_2Si(Cl)-Si(Cl)Me_2$ also gave a P-silylated diphosphadiboretane **210** that produced the first bicyclic six-atom cage **211** upon dehydrohalogenation.[67] This chemistry is summarized in Scheme 12. Attempts to prepare a derivative with $^iPr_2NB$ groups were initially unsuccessful. Instead, the reaction of $^iPr_2NBP(H)(^iPr_2N)BPLi$·DME with $Me_2Si(Cl)-Si(Cl)Me_2$ gave **212**. Further, reaction of **212** with BuLi produced small amounts of the target bicyclic **213**, as shown in Scheme 13.[67]

The generality of this stepwise assembly approach for cage syntheses has been further extended to include germane derivatives, as shown in Scheme 14. Unlike the cases shown above, the intermediate P-germylated B_2P_2 ring compound can apparently undergo either intramolecular dehydrohalogenation with formation of a cage species or intermolecular dehydrohalogenation with formation of soluble oligomers, **215**. Further examples and implications for this chemistry are being developed.

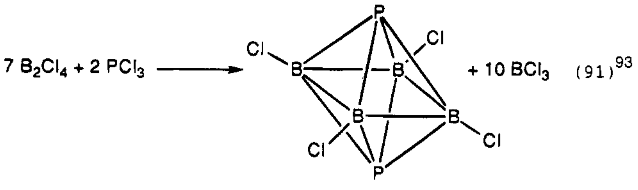
Finally, the reactions of the lithium salts $^iPr_2NBP(H)B(N^iPr_2)PLi$·DME and TmpBP(H)B(Tmp)PLi·DME with $SiCl_4$ and Si_2Cl_6 have recently been observed to produce novel spirocyclic compounds **216**, as shown in Scheme 15,[69] and an unusual "triple cage" **217**, as

Scheme 13



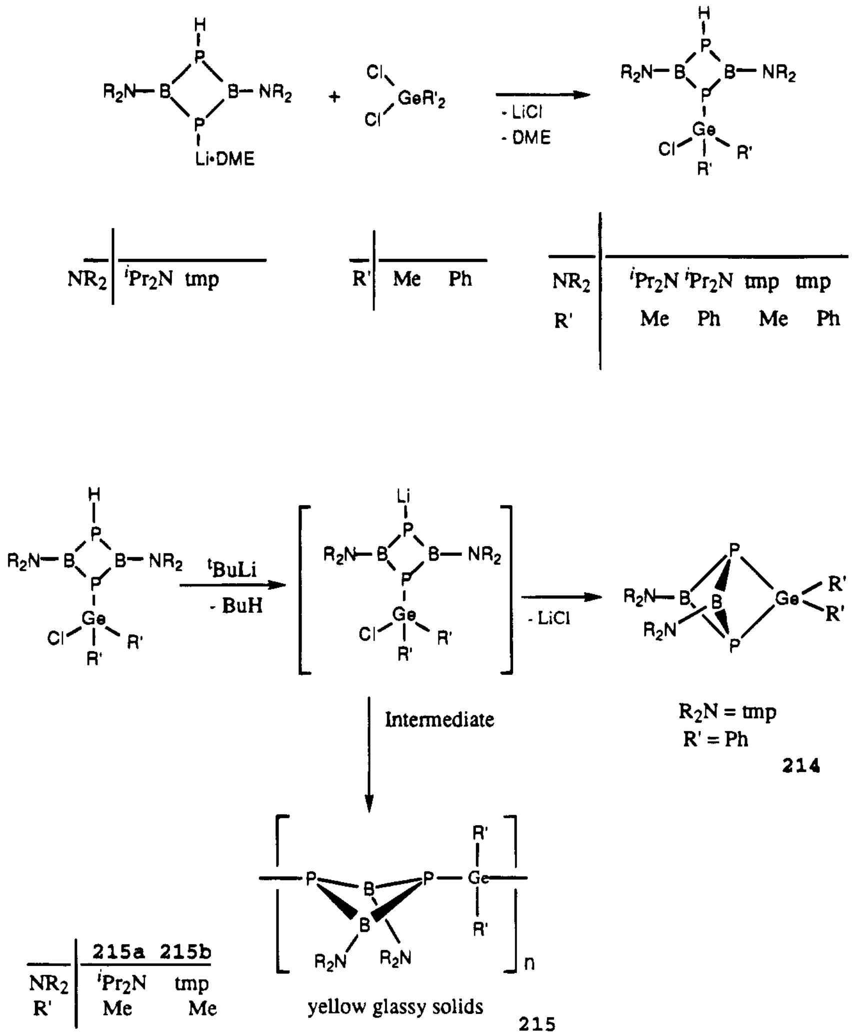
shown in Scheme 16. Although the mechanism for assembly are not yet proven, current data are consistent with pathways proposed in each scheme.

In a completely different approach to the synthesis of B−P cage compounds, Haubold and co-workers[93] found that the reaction of B_2Cl_4 and PCl_3 resulted in a *closo*-diphosphahexaborane $P_2B_4Cl_4$ (eq 91). Keller



and co-workers have also reported the formation of the corresponding bromo analog.[94]

Scheme 14



NR$_2$	^{i}Pr$_2$N	tmp

R'	Me	Ph

NR$_2$	^{i}Pr$_2$N	^{i}Pr$_2$N	tmp	tmp
R'	Me	Ph	Me	Ph

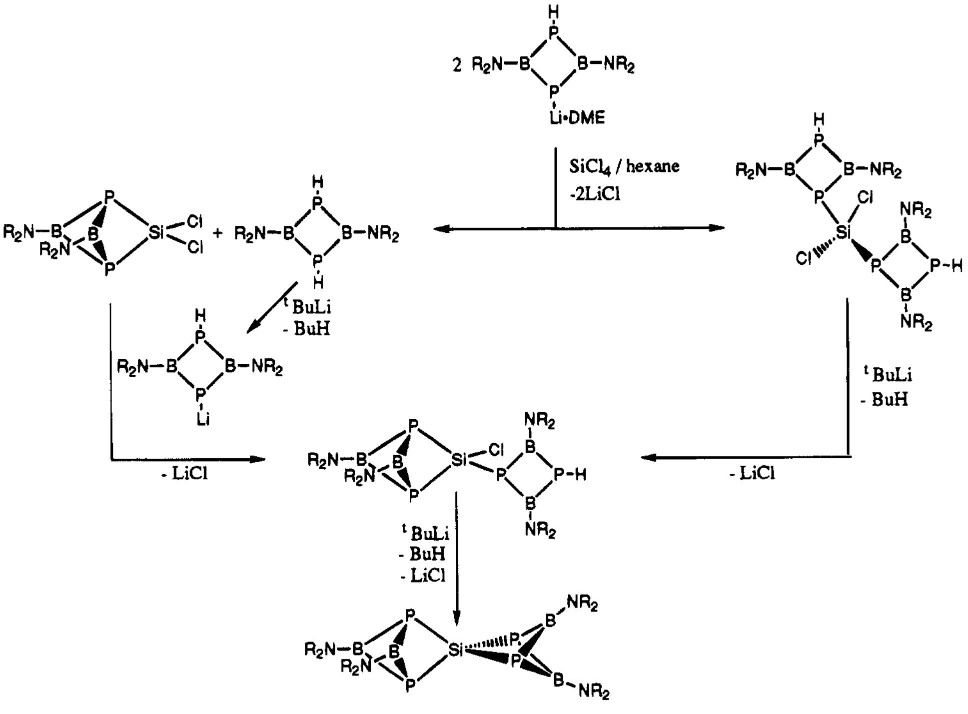
R$_2$N = tmp
R' = Ph
214

	215a	215b
NR$_2$	^{i}Pr$_2$N	tmp
R'	Me	Me

yellow glassy solids

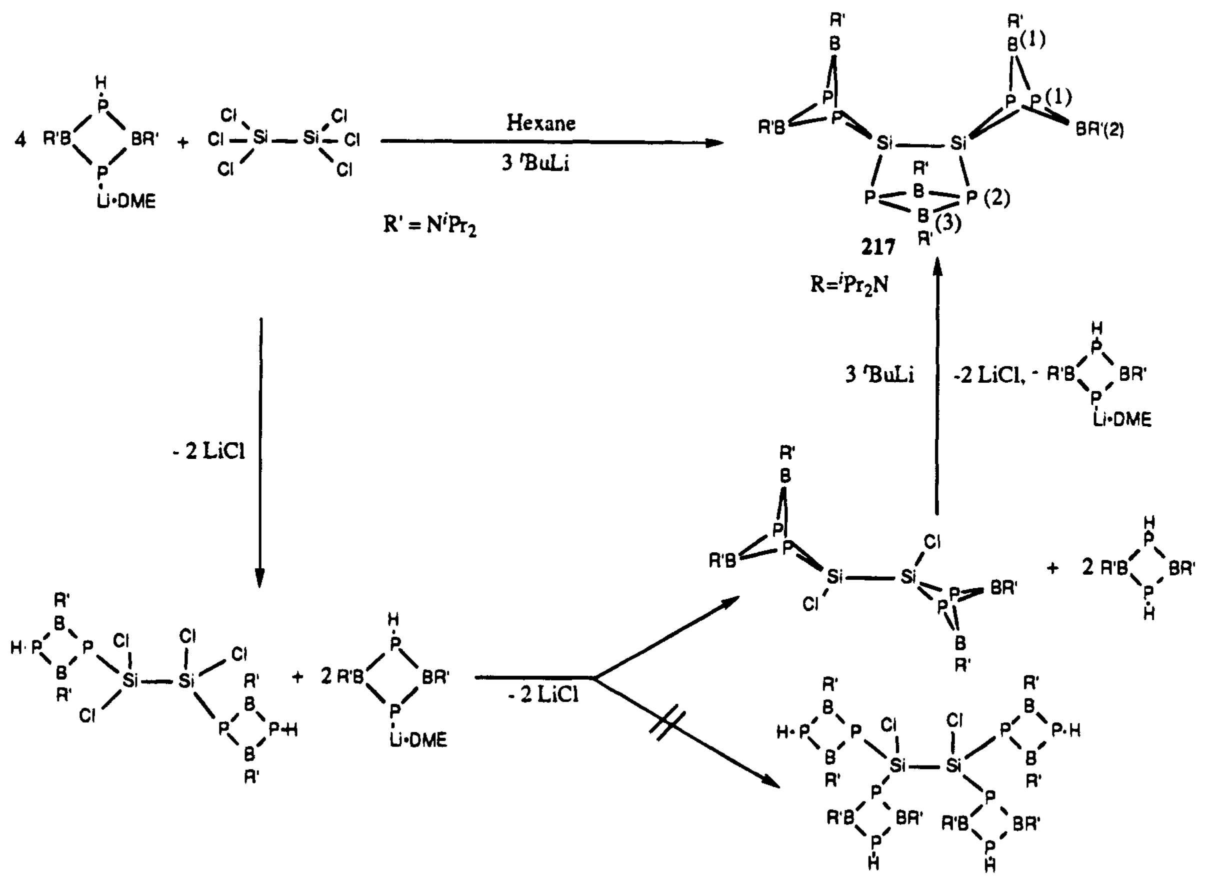
215

Scheme 15



216

Scheme 16



B. Structural Characterization

Each of the new cage compounds has been fully characterized by spectroscopic and analytical data, and $^{11}B\{^1H\}$ and $^{31}P\{^1H\}$ NMR data are summarized in Table 11. The ^{11}B chemical shifts appear in a narrow region δ 5–38 characteristic of three-coordinate aminoborane fragments. Those cages that contain inequivalent aminoborane fragments R_2NB/R'_2NB show two ^{11}B resonances in a 2:1 ratio as expected. The ^{31}P NMR chemical shift data appear over a much wider range, reflecting different P atom hybridizations. For example, the bicyclo[1.1.0]butane analogs show very high field shifts δ −290. This is consistent with the presence of the P–P bond and a small sum of bond angles about the phosphorus atoms. The remaining five- and six-atom cage compounds have ^{31}P shifts in the region δ −85 to 70.[62,67]

The molecular structure determination[50] for $(tmpBP)_2$ (**199a**) confirms the butterfly structure for the molecule, with a ring fold angle of 104.1°. The P–P bond distance, 2.349(2) Å, falls in the range expected for a single bond, and it is longer than that found in the three-membered ring compound $Et_2NB(P^tBu)_2$, 2.225(1) Å. The B–P bond distances, 1.904(6) and 1.907(5) Å, fall on the short end of the range expected for B–P single bonds.

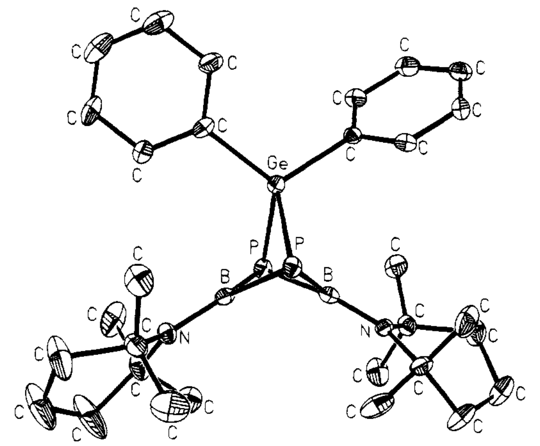


Figure 15. Molecular structure of $(TmpB)_2(Ph_2Ge)P_2$ (**214**).

The molecular structures of the B_3P_2 **200–205** and B_2SiP_2 **206–209** cage compounds are closely related.[62,67] Each molecule adopts a trigonal bipyramidal structure with the phosphorus atoms in the apical positions. The B–P bond distances are relatively long, 1.992–1.948 Å, and the sums of the angles about the phosphorus atoms are very small, 265–200°. The bicyclic six-atom cages **211** and **213** display a structure in which the B_2P_2 unit is slightly folded along the nonbonded B–B vector and the bonded Si–Si bond vector spans between the two phosphorus atoms. The B–P and Si–Si bond distances both fall in the single bond range. Each of these structures has been discussed in detail.[62,67]

The molecular structure of the P_2B_2Ge cage **214** was recently determined, and a view of the molecule is shown in Figure 15. The structure is closely comparable with the Si analogs **206** and **208**, although some strain in the cage structure may be inferred from the bond distances and internal angles. The molecular structures for the spirocycles **216a** and **216b** are shown in Figures 16 and 17.[69] Consistent with the spectroscopic data for the molecules, they

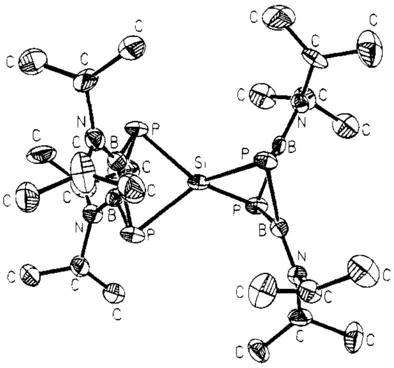


Figure 16. Molecular structure of $[(^{i}Pr_2NB)_2P_2]_2Si$ (**216a**).

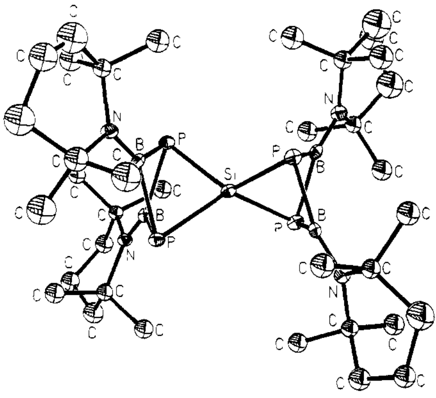


Figure 17. Molecular structure of $[(TmpB)_2P_2]_2Si$ (**216b**).

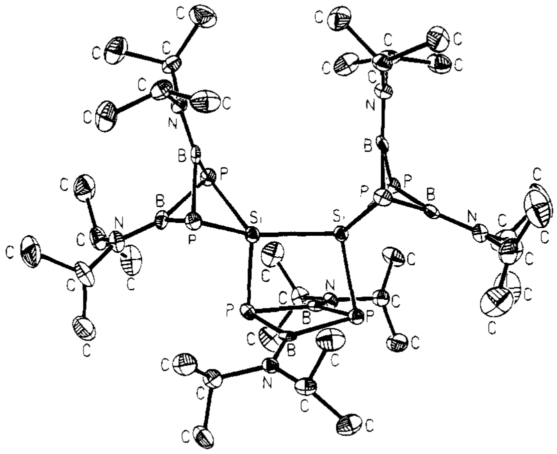


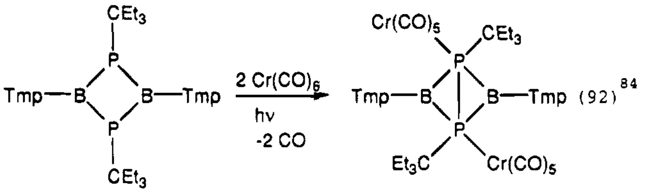
Figure 18. Molecular structure of $[(^{i}Pr_2NB)_2P_2Si]_2(^{i}Pr_2NBP)_2$ (**217**).

are found to be highly symmetrical. The two trigonal bipyramids share a common vertex occupied by the Si atom, and the B−P bond distances are 1.966 and 1.922 Å. Recently, the molecular structure of the "triple cage" compound **217** has been determined and is shown in Figure 18. The heavy atom core consists of three B_2P_2 rings interlinked by the Si atoms of the disilane. There is a wide variation in B−P distances, but the average falls in the single bond range expected from the structural analyses of the other cages.

The molecular structure of the *closo*-diphosphahexaborane $P_2B_4Cl_4$ has been determined, and it is unique in that the phosphorus atoms occupy *cis* positions in the B_4P_2 octahedron.[93] The average B−P bond distance is 2.00 Å, and the P−P bond distance is 2.222(3) Å.

C. Reaction Chemistry

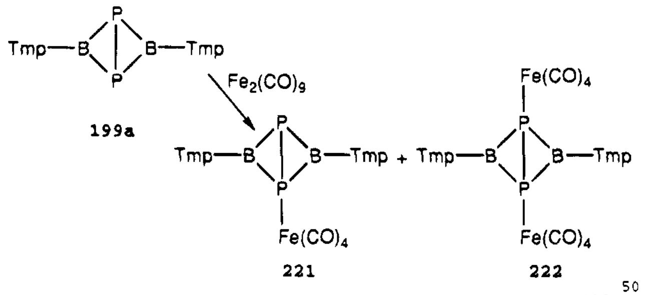
Reaction chemistry of the molecules described in this section is as yet relatively sparse, and it is generally limited to coordination chemistry. Photolysis of a mixture of the four-membered ring compound $(TmpBPCEt_3)_2$ and $Cr(CO)_6$ in pentane[84] results in the formation of a bimetallic complex **218** of the bicycle **199a** (eq 92). This reaction is not totally general. For example, reaction of **85** and **86** with $Cr(CO)_5$·THF produces the $Cr(CO)_5$ stabilized boranylidenephosphane **46** and $TmpBP(^{t}Bu)Cr(CO)_5$ (eq 17).[59,64] Combination of **74** with $Cr(CO)_6$, followed by photolysis, gives only a monometallic complex **219** of the 1,3,2,4-diphosphadiboretane. Reaction of $(Et_2NBP^{t}Bu)_2$ (**220**) with $Cr(CO)_5$·NMe_3 gives a mixture of products containing the mono- and bimetallic complexes **189** and **190** of the diphosphadiboretane (eq 80). Clearly, reaction conditions and substituent groups play a role in the formation of these various products.



(92)[84]

218

Reaction of the preformed bicycle **199a** with $Fe_2(CO)_9$ gives both monometallic **221** and bimetallic compounds **222**[95] (eq 93). These complexes have been characterized by spectroscopic and analytical data. In addition, the reactions of **199a** with $(MeCp)Mn(CO)_3$ have been studied, and mono- **223** and bimetallic **224** complexes of the bicycle have been formed (Table 12). In addition, **199b** has been combined with $(MeCp)Mn(CO)_3$, and the mono- **225** and bimetallic **226** complexes have been obtained. The molecular structure has been determined for **226**.[95]



199a **221** **222**

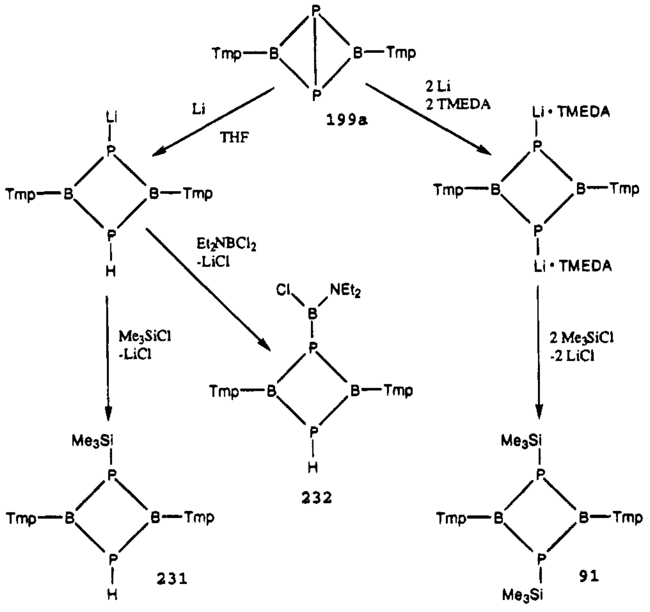
(93)[50]

The combinations of **202**−**204**, **206**−**208**, **211**, and **213** with $Cr(CO)_5(NMe_3)$ and/or $Fe_2(CO)_9$ in all cases give monometallic complexes,[62,67] and no evidence has been found for formation of dinuclear complexes. These complexes have also been characterized by spectroscopic methods and the molecular structures of $(^{i}Pr_2NB)_2(TmpB)P_2[Cr(CO)_5]$ (**227**), $(^{i}Pr_2NB)_3P_2[Fe(CO)_4]$ (**228**), $(^{i}Pr_2NB)_2(SiPh_2)P_2[Fe(CO)_4]$ (**229**), and $(TmpB)_2(SiMe_2)P_2[Fe(CO)_4]$ (**230**) have been determined by single-crystal X-ray diffraction analysis. The structural features for the cage com-

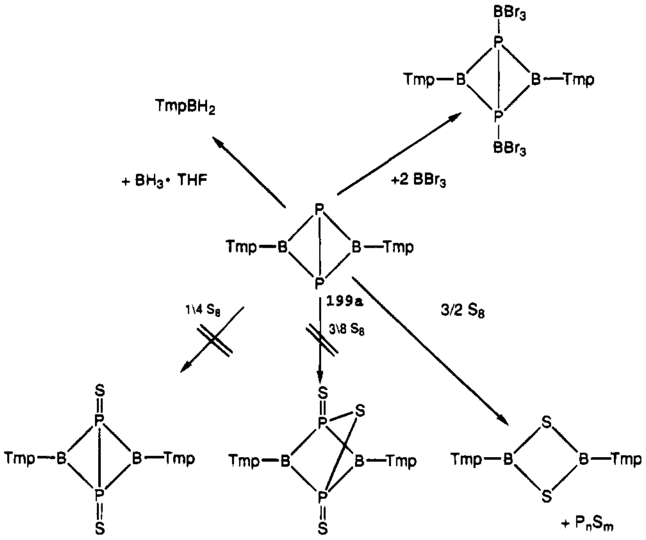
Table 12. Structural and NMR Data for Metal Carbonyl Complexes of Polycyclic Compounds

compound	bond length P–B (Å)	sum of angles at P (deg)	$\delta^{31}P$	$\delta^{11}B$	ref
$(TmpBP)_2\cdot[Cr(CO)_5]_2$ (**218**)			−180.9	40.1	84
$(TmpBP)_2\cdot Fe(CO)_4$ **221**			−142.3 −282.3	40.9	84
$(TmpBP)_2\cdot[Fe(CO)_4]_2$ (**222**)			−140.8	39.4	84
$(TmpBP)_2\cdot CpMn(CO)_2$ (**223**)			−66.7 −286.6	44.9	84
$(TmpBP)_2\cdot[CpMn(CO)_2]_2$ (**224**)			−98.7		84
$(^tBu_2NBP)_2\cdot[MeCpMn(CO)_2]$ (**225**)			−46.1 −257.7		84
$(^tBu_2NBP)_2\cdot[MeCpMn(CO)_2]_2$ (**226**)	1.905(4) 1.902(5) 1.902(4) 1.908(4)		87.8	41.3	84

Scheme 17



Scheme 18



pounds show little variation from those of the free ligands.

A small amount of other reaction chemistry has been accomplished with **199a**. For example, compound **199a** combines with only 1 equiv of Li in THF, and the resulting monolithium salt in combination with Me_3SiCl forms the P-silyl derivative **231**. Reaction with Et_2NBCl_2 produces a P-borylate species **232**. In the presence of TMEDA, **199a** reacts with 2 equiv of Li and forms a dilithio salt, and this salt undergoes double substitution, as shown in Scheme 17. The bicycle also forms a bis adduct with BBr_3, while $H_3B\cdot THF$ appears to degrade **199a** and results in formation of $TmpBH_2$ (Scheme 18). Addition of sulfur to **199a** leads to decomposition of the bicycle and formation of P_nS_m and $(TmpBS)_2$.

V. Conclusion

The expansion in interest and attention in phosphinoborane chemistry over the last seven years has resulted in a remarkable collection of new compounds with interesting structures and electronic properties. In some instances, the new classes of BP compounds have close structural and reactivity parallels with organic and boron–nitrogen analog compounds, while in many other cases the boron–phosphorus compounds represent strong departures from the lighter element chemistry. As discussed in sections II and III, many of the novel features revealed in BP compounds result from the inherently low activation energy for condensation of X_2BBY_2 and XBPY building block fragments[56,83] as well as from the polar character of the B–P σ and π bond overlaps. It has been found in recent studies that some logical control of the condensation and reactivity behavior of unsaturated BP fragments can be realized by judicious substituent group modifications. For example, delocalized boraphosphabenzenes are formed perhaps by cyclotrimerization of boranylidenephosphene fragments when sterically bulky organic substituents are present. In contrast, diphosphadiboretanes and triphosphatriborinanes having pyramidal lone-pair localized phosphorus atoms result when π-donating alkylamino groups are present on the boron atoms. Interestingly, the different electronic structures in these molecules are also revealed in their coordination chemistry. For example, the planar electron delocalized systems form metallocenes, while the nonplanar rings so far provide only simple P atom lone pair donor complexes with electron-rich metal fragments.

It can be anticipated that continued study in this area will uncover many additional parallels and contrasts between organic and inorganic systems. Further, as the systematic features become more fully understood, it can be expected that practical applications for boron–phosphorus molecular chemistry may ensue. For example, it was pointed out in 1961 that reaction of (Me$_3$Si)$_3$P with BF$_3$ and BCl$_3$ produced boron phosphide, although the material was not fully characterized.[43] Unpublished reinvestigations of these reactions, as well as reactions with BBr$_3$ and B$_2$H$_6$, confirm these findings and suggest that the solid-state material can be readily obtained. Further studies of this chemistry and other reactions in the gas and solution phases may provide access to useful films, bulk powders, and perhaps nanosized forms of pure boron phosphide.

Acknowledgments

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