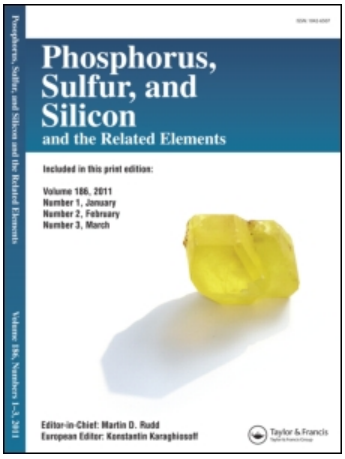

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HYDROBORATION—OXIDATION OF 1-TRIALKYLSILYL DIALKYLPHOSPHORAMIDOPROPYNES REGIOSELECTIVITY AND REACTIVITY

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The regioselectivity of the hydroboration of 1-trialkylsilyl dialkylphosphoramidopropynes was studied. The directive role of silicon was not always observed. In some cases inductive effects of substituents led to different and event opposite regioselectivity. We found here an interaction between boron and the phosphoryl group for the C2 addition which has not previously been observed. After oxidation, this interaction leads to byproducts. Understanding of the scope and limitations of this hydroboration-oxidation reaction enabled selective synthesis of the novel phosphorylated acids and ketones.

Key words: Silylated dialkylphosphoramidopropynes; hydroboration—oxidation; regioselectivity; reactivity.

The hydroboration reaction is one of the best methods for transformation of an unsaturated bond to an organic group.[1] A drawback of this widely used synthetic reaction stems from the high reactivity of borohydrides towards functional groups. Over the past two decades, a considerable body of research has been devoted to the regio and stereoselectivity of hydroboration of unsaturated compounds containing a heteroatom (oxygen, nitrogen, sulfur, silicon, halogen, etc.).[2,3] In our laboratory, we have investigated the interactions between the nitrogen atom and borohydrides,[4] and the synthetic potential of such systems, particularly from the *N*-propargylic dialkylphosphoramidates.[4b,5] The variety of reactions involving silicon, especially those employed in the preparation of compounds of biological importance led us to investigate compounds containing both nitrogen and silicon atoms. To our knowledge, there have been no reports on the hydroboration of such compounds, and relatively little work has been devoted to the hydroboration of alkynylsilanes.[6–8] The regioselectivity of the addition of boron appears to be governed in such cases by steric effects around the triple bond.[6a,7a] However, the stereochemistry of the unsaturated compound was thought by Zweiffel *et al.*[8] to govern the regioselectivity of hydroboration of 4-trimethylsilyl 1-methoxybut-1-en-3-ynes. Recently, Arase *et al.*[9] showed that the trimethylsilyl group in 3-chloro-1-trimethylsilylpropynes adds to the mesomeric effect of chlorine on addition of borohydrides (83% to 30% C_2 addition when going from n-C_4H_9 to $Si(CH_3)_3$), and thus opposes the regioselectivity induced by steric factors. Furthermore, the nature and size of the hydroboration reagent also influences these addition reactions and reduces their selectivity. The regioselectivity of the addition of borohydrides to unsaturated molecules bearing heteroatoms thus cannot be readily predicted. Nevertheless, the preparation of multifunctional organoboron derivatives of this kind opens new perspectives in organic synthesis.

In the course of research on routes of access to functional amines via hydroboration reactions we carried out a study on the addition of borohydrides to the 1-trialkylsilyldialkylphosphoramidopropynes 2.

REGIOSELECTIVITY

Synthesis of 1-Trialkylsilyl Dialkylphosphoramidopropynes 2

The sp carbon of the *N*-propargylphosphoramidates[10] is silylated to give the new compounds 2 in good yield (Table I). Only chlorosilanes can be employed, as bromosilanes tend to dealkylate the phosphoric esters.[11]

Hydroboration of Derivatives 2

Conditions for hydroboration were based on literature data,[1] and the results of previous studies in our laboratory.[4,5] Complete reaction was obtained 1 h after addition of one equivalent of dicyclohexylborane ($(Chx)_2BH$) at 10°C. It was confirmed by IR (appearance of CH=C— vibration at the expense of C≡C) and ^1H NMR (appearance of ethylenic peaks) spectroscopy. The two peak complexes of the ethylenic protons (1 triplet and 1 singlet) suggested that there had been a non-regioselective addition of boron, giving rise to compounds 4 and 5 (Table II).

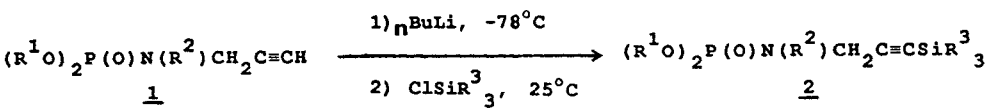


TABLE I
Synthesis of 1-trialkylsilyl dialkylphosphoramidopropynes 2

$(R^1O)_2P(O)N(R^2)CH_2C{\equiv}C\text{-}SiR^3{}_3$

Entry	R^1	R^2	R^3	Yield %	bp °C/mHg
a	C_2H_5	CH_3	CH_3	90	50/0.04
b	C_2H_5	$isoC_3H_7$	CH_3	80	60/0.04
c	C_2H_5	$CH_2C_6H_5$	CH_3	95	130/0.02
d	C_2H_5	C_6H_5	CH_3	90	120/0.02
e	C_6H_5	CH_3	CH_3	90	mp = 69°C
f	C_2H_5	CH_3	CH_3H_7	95	101/0.02
g	C_2H_5	$CH_2C_6H_5$	$isoC_3H_7$	95	165/0.02
h	C_2H_5	C_6H_5	$isoC_3H_7$	75	145/0.02
i	C_6H_5	CH_3	$isoC_3H_7$	80	140/0.01

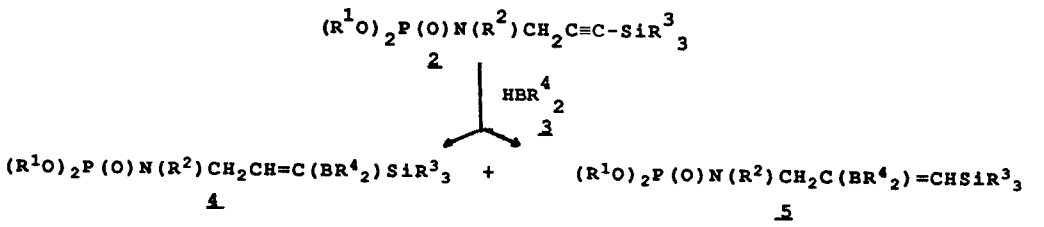
TABLE II

Influence of substituents of triple bond on the alkyne 2

$(R^1O)_2P(O)N(R^2)CH_2C{\equiv}C\text{-}SiR^3{}_3$

Entry	R^1	R^2	R^3	%4*	%5*
2a	C_2H_5	CH_3	CH_3	80	20
2b	C_2H_5	$isoC_3H_7$	CH_3	70	30
2c	C_2H_5	$CH_2C_6H_5$	CH_3	70	30
2d	C_2H_5	C_6H_5	CH_3	60	40
2e	C_6H_5	CH_3	CH_3	70	30
2f	C_2H_5	CH_3	CH_3H_7	30	70
2g	C_2H_5	$CH_2C_6H_5$	$isoC_3H_7$	25	75
2h	C_2H_5	C_6H_5	$isoC_3H_7$	20	80
2i	C_6H_5	CH_3	$isoC_3H_7$	40	60

* Percentages determined by ^1H NMR on the crude mixture



a) Influence of substituents of the alkyne (Table II). Hydroboration by the dicyclohexylborane was complete and monohydroboration was almost exclusively observed for all the phosphoramidates 2. However, the reactions of the trimethyl and triisopropylsilyl derivatives differed in their sensitivity to temperature. The trimethylsilyl compounds reacted at temperatures above 5°C, with rapid completion of the addition at 20°C, whereas for the triisopropylsilylated derivatives, the vinylborane was not observed below 20°C, and the reaction did not go to completion unless the reaction mixture was heated to 40°C (followed by ^1H NMR). The presence of a triplet (around 5.4 ppm for the trimethylsilyl and 5.8 ppm for the triisopropylsilyl derivatives) was indicative of the presence of compound 4 (C_1 addition), while the singlet (around 5 ppm) was attributed to the presence of compound 5 (C_2 addition). Unfortunately these two organoboranes could not be readily distinguished with ^{11}B NMR. Only a single broad peak around 30 ppm was observed for the mixture of compounds 4 and 5, which is in agreement with our previous observations on similar structures.[4b] However, two distinct values were obtained on analysis of the ^{31}P NMR chemical shifts of these hydroboration products (Table III).

The two ^{31}P NMR chemical shifts can be attributed to the presence of two

organoboranes (compounds 4 and 5). The chemical shifts (Table III) were attributed on the basis of their similarity to those of similar structures,[4d] and by comparing the relative percentages of the two forms with those observed on ^1H NMR (Table II). The shielding observed in the chemical shift of the phosphorus peak of compounds 5 (C_2 addition) could be accounted for by the proximity of boron as acceptor, giving rise to a phosphoryl (P=O)-boron interaction. The *cis* addition of borohydrides prevents this interaction in compounds 4 (C_1 addition).

It should also be noted that on hydroboration by dithexylborane ($(Thx)_2BH$) or diisopinocampheylborane (Ipc_2BH) the same differences in chemical shifts were observed for the corresponding complexes 4 and 5 in the ^{31}P NMR (cf. Table III). A further example of this phenomenon was observed in the hydroboration of

TABLE III

^{31}P NMR chemical shifts of hydroboration products

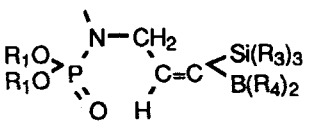
Entry	Hydroboration of 2 with				
	Alkyne	$(Chx)_2BH$		Ipc_2BH	
	2	4**	5	4**	5
a	9.79	10.53 (80)	9.02 (20)	10.6 (40)	9.05 (60)
b	9.65	10.22 (70)	8.8 (30)		
c	9.55	10.03 (70)	8.7 (30)		
d	5.49	5.9 (60)	4.7 (40)		
e	0.42	0.91 (70)	0.02 (30)		
f	9.47	9.9 (30)	9.2 (70)	***	9.94 (90)
g	9.16	9.72 (20)	8.85 (80)		
h	5.10	5.53 (40)	4.90 (60)		
i	-0.03	0.8 (40)	- 0.21 (60)		

* figures in brackets are relative percentages

** $(C_2H_5O)_2P(O)N(CH_3)CH_2CH{=}CHB(C_6H_{11})_2$: δ (ppm) 10.3 ($^{31}P$) and 31.6 ($^{11}B$)

$(C_2H_5O)_2P(O)N(CH_3)CH_2CH{=}CHBIpc_2$: δ (ppm) 10.56 ($^{31}P$)

*** not visible on spectrum



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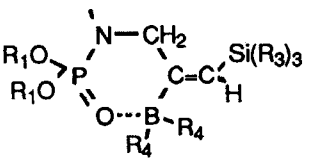


5

compound 2f by diisopinocampheylborane (Ipc_2BH) giving rise to a single visible peak in the ^{31}P NMR in agreement with 90% formation of 5f. The mass spectra of the hydroboration products also support our hypothesis. The mixture of the isomeric vinylorganoboranes 4c and 5c from hydroboration by dicyclohexylborane ($(Chx)_2BH$) of the alkyne 2c gives rise to a single mass peak of 552 (4c or 5c $C_{31}H_{47}O_3PNSiB$: m = 551.6). This value is in agreement with monoboration. Analysis of the fragmentation peaks showed that there was successive loss of two cyclohexyl groups, indicating, as had been suggested by the ^{31}P NMR findings (Table III), that they were not equivalent.

b) Influence of the hydroboration agent (Table IV). The nature of the hydroboration agent affects both the extent of the addition reaction (chemical reactivity) and the regioselectivity of the addition (orientation) (Table IV). It is noteworthy that no reaction occurred with 9-BBN and $(Mes)_2BH$ under all experimental conditions tested, despite the known affinity of these two reagents for alkynes.[12]

Discussion

Although we observed the steric effects of the trimethylsilyl and triisopropylsilyl groups reported for the alkynylsilanes,[6,7] any interpretation of our results must also take account of electronic effects induced by the phosphoramidomethyl groups and the silicon atom. This can explain the relative percentages of compounds 4 and 5

TABLE IV

Influence of the hydroboration agent

Hydroboration* agents		$(C_2H_5O)_2P(O)N(R^2)CH_2C{\equiv}C\text{-}SiMe_3$ 2a(R^2 = CH^3)				$(C_2H_5O)_2P(O)N(R^2)CH_2C{\equiv}C\text{-}Si(isoC_3H_7)_3$ 2f (R^2 = CH^3)		
		Hydroboration products						
	Entry	% 4**	% 5**	Yield %	Entry	% 4**	% 5**	Yield %
$(Chx)_2BH$	a	80	20	100	f	30	70	100
Sia_2BH	l	80	20	100	p	30	70	100
$(Thx)_2BH$	m	40	60	70	r	10	90	80
Ipc_2	n	40	60	70	s	10	90	80
9-BBN		-	-	0		-	-	0
$(Mes)_2BH$		-	-	0		-	-	0

* abbreviations: $(Chx)_2BH$ = dicyclohexylborane; Sia_2BH = disiamylborane; $(Thx)_2BH$ = dithexylborane; Ipc_2 = diisopinocampheylborane; 9-BBN = 9-borabicyclononane; $(Mes)_2BH$ = dimesitylborane

** percentages determined by ^1H NMR on the crude mixture

for almost identical steric hindrance. We also found that replacement on the nitrogen atom of the methyl with a phenyl group, despite the increased steric hindrance, consistently favored C_2 addition. An identical effect was observed on replacement of the ethyl ester $(C_2H_5O)_2P(O)$ by the phenyl ester $(C_6H_5O)_2P(O)$. However this effect was not observed for the triisopropylsilyl compounds. The regioselectivity of these additions is thus not readily predicted. Neither steric nor electronic effects predominate and the regioselectivity will be determined by the resultant of their interaction.

An interaction between the phosphoryl group (P=O) and boron may also be fostered by the silicon atom. In previous experimentation, we found that phosphorated compounds such as hexamethylphosphoramidate (HMPT) and the *N*-propargylic dialkylphosphoramidates do not complex with dialkylboranes.[4b] The electropositive character of silicon may thus compete with that of boron for the electron-rich unsaturated sites. In this case, boron will tend to be attracted by the electrons on the neighboring phosphoryl group (P=O), which could account for some of the reactions of these new organoboranes.

REACTIVITY

Oxidation of these vinylboranes normally gives rise to a carbonyl derivatives 6 and 7.[2] The results are listed in Table V and illustrated in the Scheme I. The complete disappearance of the vinylboranes 4 and 5 (followed by ^1H and ^{11}B NMR) indicated that the oxidation was complete.

The yields of acids 6 were in agreement with the percentages of the organoboranes form 4 (figures in brackets in Table V). Oxidation of compounds 4 proceeds thus as expected in accordance with our previous results.[13] On the other hand, the various by-products 8, 9 and 10 obtained duration extraction of the alkaline phase were indicative of an unusual reactivity of the organoboranes 5 that we have not expected. Furthermore, the nature of the trialkylsilyl group was found to have an influence on by-product formation.

a) Reactions with trimethylsilyl compounds 2a–e. Reports of hydroboration-oxidation of alkynylsilanes[7,14] describe access to the corresponding carbonyl deriva-

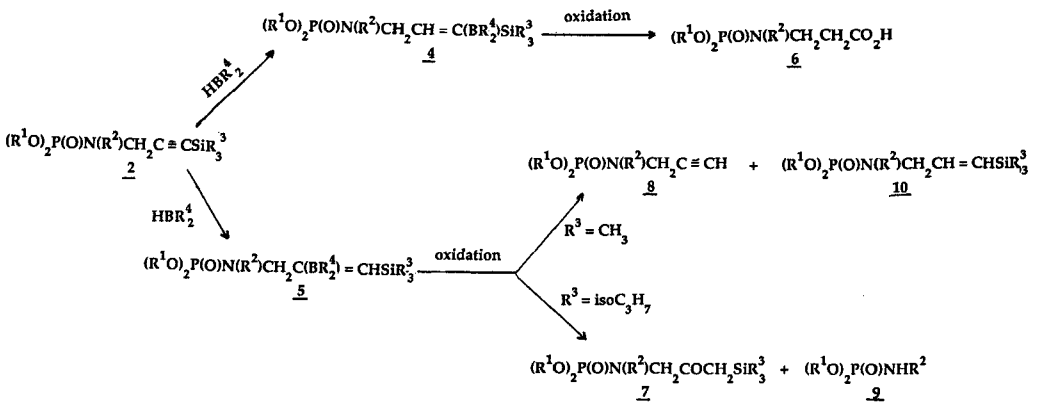
TABLE V

Hydroboration-oxidation of compounds 2 by $(Chx)_2BH$ and H_2O_2—NaOH

$R^1O)_2P(O)N(R^2)CH_2C\equiv C\text{-}SiR^3{}_3$				Acid phase*	Basic phase*			
Entry	R^1	R^2	R^3	% acid 6	% ketone 7	% C=C 10	% C≡CH 8	% $(R^1O)_2P(O)N<$ 9
a	C_2H_5	CH_3	CH_3	80 (80)**	trace	6	10	trace
b	C_2H_5	$isoC_3H_7$	CH_3	70 (70)	trace	9	12	trace
c	C_2H_5	$CH_2C_6H_5$	CH_3	70 (70)	trace	2	20	trace
d	C_2H_5	C_6H_5	CH_3	60 (60)	trace	8	18	trace
e	C_6H_5	CH_3	CH_3	60 (60)	trace	9	12	trace
f	C_2H_5	CH_3	$isoC_3H_7$	30 (30)	45	trace	trace	20
g	C_2H_5	$CH_2C_6H_5$	$isoC_3H_7$	25 (25)	50	trace	trace	10
h	C_2H_5	C_6H_5	$isoC_3H_7$	20 (20)	60	trace	trace	15
i	C_6H_5	CH_3	$isoC_3H_7$	20 (20)	30	trace	trace	25

* percentages determined by GLC and ^1H NMR

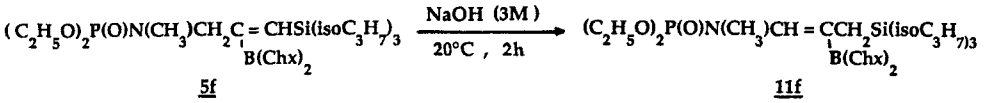
** figures in brackets are percentages of the organovinyl boranes 4



tives without mention of by-product formation. The organoboranes 5a–e are the only reactive species in the absence of starting compound or dihydroboration. Unexpectedly, no protonolysis or elimination was observed in the reaction of compounds 4a and 5a with aqueous sodium hydroxide (3 M) either in the cold or under reflux for 30 min. Given that the borates formed are more sensitive to basic media than the alkenylboranes[14] the side reactions were assumed to take place after oxidative attack and be favored by boronophosphoryl interactions, which we had previously observed with compounds 4. The acetylenic derivatives 8a–e could in principle be formed via several different routes. Since the hydroboration reaction went to completion, they could not have been produced by simple desilylation of unreacted compounds 2a–e. Furthermore, derivatives 8a–e are not formed from 10a–e in basic oxidizing medium, and there also was no evidence of dihydroboration, the remaining possibility was β-borodesilylation from the oxidized derivatives 5a–e. To our knowledge this is the first example of basic β-elimination of a vinyl borane without α-migration of one of the boron substituents. It is also of interest that we did not detect the presence of dialkylphosphoramido acetones which are formed in basic oxidizing medium from the rather unstable α-trimethylsilyl substituted ketone intermediates 7a–e. The reaction proceeds from the alkenylboranes 5a–e. The compounds 10a–e were obtained exclusively in the *cis* configuration (J_{H-H} = 12 Hz).[14d,16]

b) Reactions with triisopropyl derivatives 2f–i. The corresponding vinylorganoboranes were less sensitive to oxidation than their trimethylsilyl analogs as they led to the expected ketones 7f–i with no products of protonolysis or elimination. Unfortunately, the yield of ketone was reduced by the presence of a new by-product, the phosphoramidate 9. This derivative had previously been detected on hydroboration-oxidation of the *N*-alkyl and *N*-propargyl dialkylphosphoramidates.[5] We found that treatment with 3 *N* sodium hydroxide at room temperature transformed the phosphoramidovinylborane 5f into the enaminovinylborane 11f.

Acid hydrolysis of compounds 11f led to the phosphoramidate 9[17] as we observed in basic oxidizing medium. This shows that the sequence 5f–i → 11f–i → 9 is in competition with the normal oxidation of 5f–i to the ketone 7f–i. This oxidative route could thus be favored by reducing the basicity of the medium. This has been



5f 11f

IR = 1590cm-1
^{1}H NMR δ = 5.1 ppm
^{13}C NMR δ = 9.2 ppm

IR = 1695 cm-1
^{1}H NMR δ = 4.2 ppm
^{13}C NMR δ = 12.3 ppm

TABLE VI

Hydroboration-oxidation of compounds 2 by $(Chx)_2BH$ and various oxidizing agents*

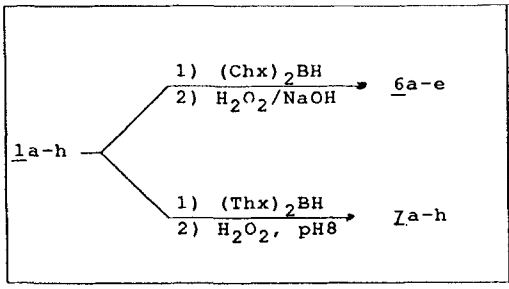
Oxidizing	Compounds	% acid	% ketone	% C=C	phosphoramidate
	1	6	7	10	9
	a	80	9	11	0
	d	60	31	9	0
$NaBO_3$,	e	62	20	10	0
nH_2O	f	30	55	0	10
	g	25	55	0	17
	h	20	67	0	10
	i**	18	40	0	15
	a	75	8	12	0
pH ~ 8	d	60	30	9	0
NaOAc	e	62	20	10	0
H_2O_2	f	30	55	0	10

* percentages determined by ^{1}H NMR

** partial hydrolysis of the phosphoric ester

TABLE VII

Selective synthesis of the acids



entry	% acid 6	entry	% ketone 7
a	55	a	38
b	55	d	45
c	60	f	60
d	60	g	65
e	55	h	63

* percentage isolated product

employed by several workers as a method of protection of the oxidation products formed,[10] but till now it was never applied for hydroboration-oxidation of alkynylsilanes. The results listed in Table VI indicate the value of this approach. We obtained identical results with the other borohydrides.

Knowledge of the limitations of this hydroboration-oxidation reaction enabled us to prepare selectively the phosphorylated acids 6 and ketones 7 (Table VII).

CONCLUSION

The presence of a phosphoramidomethyl group in alkynylsilanes complicates prediction of the regioselectivity of hydroboration. We not found here the total directing effects attributed to the trialkylsilyl groups. Furthermore, the interaction between boron and the phosphoryl group, which has not previously been observed, gives rise to secondary products in hydroboration-oxidation reactions especially borodesilylation in basic medium which are not produced from alkynylsilanes. The synthesis of these by-products is suppressed by reducing the basicity of the oxidizing medium. The phosphorylated acids and ketones could thus be synthesized selectively, with good yield.

EXPERIMENTAL

^1H, ^{13}C and ^{31}P NMR spectra were recorded on Brucker 80 or Brucker 200 instruments. The IR spectra were recorded on a Perkin Elmer 683 spectrophotometer. Purification by gas chromatography was carried out on an Intersmat IGC 120F apparatus fitted with a SE 20 (1.50 m) column. Melting points were uncorrected, and were determined on a digital Koffler block.

1-trialkylsilyl-3-dialkylphosphoramidopropynes 2.

Typical procedure: synthesis of 2a. A solution of n-BuLi (2.5 M in hexane: 4.8 ml, 0.012 mol) is added to a solution of *N*-methyl *N*-propargyl diethylphosphoramidate 1a (2.05 g, 0.01 mol) in anhydrous THF (10 ml) with stirring at −78°C. The reaction mixture is maintained under constant agitation at −78°C for 30 min. Trimethylsilyl chloride (1.5 ml, 0.012 mol) is added, the reaction is maintained at −78°C for a further 30 min, and then the mixture is allowed to rise slowly to ambient temperature. It is left for a further 1 h at ambient temperature. It is hydrolyzed with 20 ml of distilled water, and extracted with chloroform (3 × 20 ml). The organic phases are washed with distilled water (2 × 20 ml), dried (Na_2SO_4), concentrated under vacuum and purified by distillation (2.5 g, 0.009 mol) (Table I).

For the physical characteristics of 2a–i see Table I. The physical and spectral characteristics of compounds 2a–e were in agreement with literature data.[13] Compounds 2f–i were new.

Spectral characteristics of 2f–i.

Compound 2f $(C_2H_5O)_2P(O)N(CH_3)CH_2C{\equiv}CSi(isoC_3H_7)_3$: Yield = 95%
IR film ν (cm^{-1}): 2180 (C≡C), 1230 (P=O), 1260 (C—Si), 1030 (P—O—C)
^1H NMR ($CDCl_3$/TMS) δ (ppm) J (Hz): 0.99 (d, 18H, CH_3), 1.1 (m, 3H, CH—Si), 1.2 (t, 6H, CH_3, J_{H-H} = 5.25), 2.6 (d, 3H, N—CH_3, J_{P-H} = 8.7), 3.75 (d, 2H, N—CH_2, J_{P-H} = 7.9), 4.0 (q.d, 4H, CH_2—O, J_{P-H} = 7.9, J_{H-H} = 5.2)
^{13}C NMR ($CDCl_3$/TMS) δ (ppm): 11.11 (CH of isoPr), 16.3 (CH_3), 18.4 (CH_3 of isoPr), 33.4 (N—CH_3), 40.6 (N—CH_2), 62.3 (CH_2—O), 77.2 (C≡), 85.2 (≡CSi)
^{31}P NMR ($CDCl_3$/H_3PO_4): 9.5
% Anal for $C_{17}H_{36}O_3PNSi$: Found C 56.41, H 10.07, N 3.90; Calc. C 56.48, H 10.04, N 3.87

Compound 2g $(C_2H_5O)_2P(O)N(CH_2C_6H_5)CH_2C{\equiv}CSi(isoC_3H_7)_3$: Yield = 95%
IR film ν (cm^{-1}): 2180 (C≡C), 1230 (P=O), 1260 (C—Si), 1030 (P—O—C)

^{1}H NMR ($CDCl_3$/TMS) δ (ppm) J (Hz): 0.99 (d, 18H, CH_3), 1.1 (m, 3H, CH—Si), 1.2 (t, 6H, CH_3, J_{H-H} = 5.25), 3.7 (d, 2H, N—CH_2, J_{P-H} = 7.9), 4.0 (q.d, 4H, CH_2—O, J_{P-H} = 7.7, J_{H-H} = 5.2), 4.2 (d, 2H, N—CH_2—C_6H_5, J_{H-P} = 8.9), 7.2 (m, 5H, C_6H_5)
^{13}C NMR ($CDCl_3$/TMS) δ (ppm): 11.1 (CH of isoPr), 16.3 (CH_3), 18.1 (CH_3 of isoPr), 40.6 (N—CH_2), 41.2 (N—CH_2—C_6H_5), 62.3 (CH_2—O), 77.2 (C≡), 85.1 (≡CSi), 120 and 150 (m, C_6H_5) ^{31}P NMR ($CDCl_3$/H_3PO_4): 9.16
% Anal for $C_{23}H_{40}O_3PNSi$: Found C 63.02, H 9.26, N 3.12; Calc. C 63.12, H 9.21, N 3.20

Compound 2h $(C_2H_5O)_2P(O)N(C_6H_5)CH_2C{\equiv}CSi(isoC_3H_7)_3$: Yield = 75%
IR film ν (cm^{-1}): 2180 (C≡C), 1230 (P=O), 1260 (C—Si), 1030 (P—O—C)
^{1}H NMR ($CDCl_3$/TMS) δ (ppm) J (Hz): 0.99 (d, 18H, CH_3), 1.1 (m, 3H, CH—Si), 1.2 (t, 6H, CH_3, J_{H-H} = 5.2), 3.7 (d, 2H, N—CH_2, J_{P-H} = 7.9), 4.0 (q.d, 4H, CH_2—O, J_{P-H} = 7.7, J_{H-H} = 5.2), 7.2 (m, 5H, C_6H_5)
^{13}C NMR ($CDCl_3$/TMS) δ (ppm): 11.1 (CH of isoPr), 16.3 (CH_3), 18.2 (CH_3 of isoPr), 40.6 (N—CH_2), 62.3 (CH_2—O), 77.2 (C≡), 85.1 (≡CSi), 120 and 150 (m, C_6H_5)
^{31}P NMR ($CDCl_3$/H_3PO_4): 5.1
% Anal for $C_{22}H_{38}O_3PNSi$: Found C 62.40, H 9.12, N 3.24; Calc. C 62.38, H 9.04, N 3.31

Compound 2i $(C_6H_5O)_2P(O)N(CH_3)CH_2C{\equiv}CSi(isoC_3H_7)_3$: Yield = 80%
IR film ν (cm^{-1}): 2180 (C≡C), 1230 (P=O), 1260 (C—Si), 1030 (P—O—C)
^{1}H NMR ($CDCl_3$/TMS) δ (ppm) J (Hz): 0.99 (d, 18H, CH_3), 1.1 (m, 3H, CH—Si), 2.8 (d, 3H, N—CH_2, J_{P-H} = 8.9), 3.9 (d, 2H, N—CH_2, J_{P-H} = 7.8), 7.2 (m, 5H, C_6H_5)
^{13}C NMR ($CDCl_3$/TMS) δ (ppm): 11.11 (CH of isoPr), 18.4 (CH_3 of isoPr), 33.2 (N—CH_3), 39.5 (N—CH_2), 77.2 (C≡), 85.1 (≡CSi), 120 and 150 (m, C_6H_5)
^{31}P NMR ($CDCl_3$/H_3PO_4): −0.03
% Anal for $C_{25}H_{36}O_3PNSi$: Found C 65.53, H 7.98, N 3.10; Calc. C 65.62, H 7.93, N 3.06

Hydroboration of compounds 2. All experiments were carried out under an atmosphere of nitrogen using predried glassware. The various borohydrides were prepared as described in the literature.[1]

Typical procedure for hydroboration of 2a–e. A freshly prepared solution of borohydride (0.01 mol, 10 ml THF) is added to 0.01 mol of compound 2a–e in 10 ml of THF at 0°C. The mixture is kept at 0°C for 30 min, and then left to rise to room temperature. After stirring for 1 h, the solution is concentrated. The phosphoramidovinylboranes are recovered quantitatively as non-distillable viscous oils (Table II). The purity as checked by TLC ($CHCl_3$/hexane, 6/1) was adequate for analysis by mass, NMR and IR spectroscopy.[19]

Hydroboration of 2a–e *with dicyclohexylborane* $(Chx)_2BH$

Compound 4a $(CH_2H_5O)_2P(O)N(CH_3)CH_2CH{=}C(Si(CH_3)_3)B(C_6H_{11})_2$: Yield = 80%
IR film ν (cm^{-1}): 1590 (C=C), loss of band at 2120 (C≡C)
^{1}H NMR ($CDCl_3$/TMS) δ (ppm) J (Hz): 0.08 (s, 9H, CH_3), 1.26 (t, 6H, CH_3, J_{H-H} = 5.25), 1.5 (m, 22H, C_6H_{11}), 2.54 (d, 3H, N—CH_3, J_{P-H} = 8.9), 3.68 (d.d, 2H, N—CH_2, J_{P-H} = 7.7, J_{H-H} = 5.25), 3.9 (q.d, 4H, O—CH_2, J_{P-H} = 7.7, J_{H-H} = 5.2), 5.5 (t, 1H, CH=, J_{H-H} = 5.25)
^{31}P NMR ($CDCl_3$/H_3PO_4) δ (ppm): 10.53
^{13}C NMR ($CDCl_3$) δ (ppm): 0.95 (CH_3—Si), 16.0 (CH_3—CH_2—O), 26.9–27.7 (CH_2 of C_6H_{11}), 33.1 (N—CH_3), 36.6 (CH of C_6H_{11}), 51.6 (N—CH_2), 61.9 (O—CH_2), 134.8 (CH=), 156.0 (=CBSi)

Compound 5a $(C_2H_5O)_2P(O)N(CH_3)CH_2CB(C_6H_{11})_2{=}CHSi(CH_3)_3$: Yield = 20%
IR film ν (cm^{-1}): 1590 (C=C), loss of band at 2100 (C≡C)
^{1}H NMR ($CDCl_3$/TMS) δ (ppm) J (Hz): 0.03 (s, 9H, CH_3), 1.3 (t, 6H, CH_3, J_{H-H} = 5.2), 1.5 (m, 22H, C_6H_{11}), 2.6 (d, 3H, N—CH_3, J_{P-H} = 8.9), 3.75 (d, 2H, N—CH_2, J_{P-H} = 7.7), 3.9 (q.d, 4H, O—CH_2, J_{P-H} = 7.7, J_{H-H} = 5.2), 5.1 (s, 1H, CH=)
^{31}P NMR ($CDCl_3$/H_3PO_4) δ (ppm): 9.02
^{13}C NMR ($CDCl_3$) δ (ppm): 0.3 (CH_3—Si), 15.9 (CH_3—CH_2—O), 26.9–27.7 (CH_2 of C_6H_{11}), 33.5 (N—CH_3), 34.8 (CH of C_6H_{11}), 52.6 (N—CH_2), 61.8 (O—CH_2), 126.1 (=CH—Si), 169.2 (=CB)

Compound 4b $(C_2H_5O)_2P(O)N(isoC_3H_7)CH_2CH{=}C(Si(CH_3)_3)B(C_6H_{11})_2$: Yield = 75%
IR film ν (cm^{-1}): 1590 (C=C), loss of band at 2120 (C≡C)
^{1}H NMR ($CDCl_3$/TMS) δ (ppm) J (Hz): 0.09 (s, 9H, CH_3), 1.1 (d, 6H, CH_3, J_{H-H} = 6.7), 1.27 (t, 6H, CH_3, J_{H-H} = 5.25), 1.5 (m, 22H, C_6H_{11}), 3.6 (d.d, 2H, N—CH_2, J_{P-H} = 7.7, J_{H-H} = 5.9), 3.7 (m, 1H, CH—N), 3.9 (q.d, 4H, O—CH_2, J_{P-H} = 7.7, J_{H-H} = 5.25), 5.4 (t, 1H, CH=, J_{H-H} = 5.9)
^{31}P NMR ($CDCl_3$/H_3PO_4) δ (ppm): 10.22
^{13}C NMR ($CDCl_3$) δ (ppm): 0.9 (CH_3—Si), 16.1 (CH_3—CH_2—O), 26.9–27.8 (CH_2 of C_6H_{11}), 36.6 (CH of C_6H_{11}), 51.6 (N—CH_2), 61.9 (O—CH_2), 70.0 (CH—N), 134.8 (CH=), 156.1 (=CBSi)

Compound 5b $(C_2H_5O)_2P(O)N(isoC_3H_7)CH_2CB(C_6H_{11})_2{=}CHSi(CH_3)_3$: Yield = 25%
IR film ν (cm^{-1}): 1595 (C=C), loss of band at 2120 (C≡C)
^1H NMR ($CDCl_3$/TMS) δ (ppm) J (Hz): 0.03 (s, 9H, CH_3), 1.1 (d, 6H, CH_3, J_{H-H} = 6.7), 1.3 (t, 6H, CH_3, J_{H-H} = 5.2), 1.5 (m, 22H, C_6H_{11}), 3.6 (m, 1H, CH—N), 3.75 (d, 2H, N—CH_2, J_{P-H} = 7.7), 4.0 (q.d, 4H, O—CH_2, J_{P-H} = 7.7, J_{H-H} = 5.2), 5.1 (s, 1H, CH=)
^{31}P NMR ($CDCl_3/H_3PO_4$) δ (ppm): 8.8
^{13}C NMR ($CDCl_3$) δ (ppm): 0.3 (CH_3—Si), 15.9 (CH_3—CH_2—O), 16.1 (CH_3 of C_3H_7), 26.9–27.7 (CH_2 of C_6H_{11}), 34.8 (CH of C_6H_{11}), 52.6 (N—CH_2), 61.8 (O—CH_2), 126.1 (=CHSi), 169.2 (=CB)

Compound 4c $(C_2H_5O)_2P(O)N(CH_2C_6H_5)CH_2CH{=}C(Si(CH_3)_3)B(C_6H_{11})_2$: Yield = 70%
IR film ν (cm^{-1}): 1590 (C=C), loss of band at 2100 (C≡C)
^1H NMR ($CDCl_3$/TMS) δ (ppm) J (Hz): 0.09 (s, 9H, CH_3), 1.27 (t, 6H, CH_3, J_{H-H} = 5.25), 1.5 (m, 22H, C_6H_{11}), 3.6 (d.d, 2H, N—CH_2, J_{P-H} = 7.7, J_{H-H} = 5.2), 3.9 (q.d, 4H, O—CH_2, J_{P-H} = 7.7, J_{H-H} = 5.2), 4.2 (d, C_6H_5—CH_2—N, J_{P-H} = 8.5), 5.4 (t, 1H, CH=, J_{H-H} = 5.2), 7.2 (m, 5H, C_6H_5)
^{31}P NMR ($CDCl_3/H_3PO_4$) δ (ppm): 10.03
^{13}C NMR ($CDCl_3$) δ (ppm): 0.9 (CH_3—Si), 16.0 (CH_3—CH_2—O), 26.9–27.3 (CH_2 of C_6H_{11}), 41.1 (N—CH_2—C_6H_5), 51.6 (N—CH_2), 61.9 (O—CH_2), 127–141 (m, C_6H_5), 134.8 (CH=), 156.1 (=CSiB)

Compound 5c $(C_2H_5O)_2P(O)N(CH_2C_6H_5)CH_2CB(C_6H_{11})_2{=}CHSi(CH_3)_3$: Yield = 30%
IR film ν (cm^{-1}): 1595 (C=C), loss of band at 2120 (C≡C)
^1H NMR ($CDCl_3$/TMS) δ (ppm) J (Hz): 0.03 (s, 9H, CH_3), 1.3 (t, 6H, CH_3, J_{H-H} = 5.2), 1.5 (m, 22H, C_6H_{11}), 3.75 (d, 2H, N—CH_2, J_{P-H} = 7.7), 4.0 (q.d, 4H, O—CH_2, J_{P-H} = 7.7, J_{H-H} = 5.2), 4.2 (d, C_6H_5—CH_2—N, J_{P-H} = 8.6), 5.1 (s, 1H, CH=), 7.25 (m, 5H, C_6H_5)
^{31}P NMR ($CDCl_3/H_3PO_4$) δ (ppm): 8.7
^{13}C NMR ($CDCl_3$) δ (ppm): 0.3 (CH_3—Si), 15.9 (CH_3—CH_2—O), 26.9–27.7 (CH_2 of C_6H_{11}), 34.8 (CH of C_6H_{11}), 41.1 (N—CH_2—C_6H_5), 51.6 (N—CH_2), 61.8 (O—CH_2), 126.1 (=CH—Si), 127–141 (m, C_6H_5), 169.2 (=CB)

Compound 4d $(C_2H_5O)_2P(O)N(C_6H_5)CH_2CH{=}CSi(CH_3)_3B(C_6H_{11})_2$: Yield = 60%
IR film ν (cm^{-1}): 1595 (C=C), loss of band at 2120 (C≡C)
^1H NMR ($CDCl_3$/TMS) δ (ppm) J (Hz): 0.08 (s, 9H, CH_3), 1.26 (t, 6H, CH_3, J_{H-H} = 5.2), 1.5 (m, 22H, C_6H_{11}), 3.67 (d.d, 2H, N—CH_2, J_{P-H} = 7.7, J_{H-H} = 5.2), 3.9 (q.d, 4H, O—CH_2, J_{P-H} = 7.7, J_{H-H} = 5.25), 5.45 (t, 1H, CH=, J_{H-H} = 5.2), 7.1 (m, 5H, C_6H_5)
^{31}P NMR ($CDCl_3/H_3PO_4$) δ (ppm): 5.9
^{13}C NMR ($CDCl_3$) δ (ppm): 0.9 (CH_3—Si), 16.1 (CH_3—CH_2—O), 26.9–27.7 (CH_2 of C_6H_{11}), 36.6 (CH of C_6H_{11}), 51.6 (N—CH_2), 61.9 (O—CH_2), 127–141 (m, C_6H_5), 134.2 (CH=), 156.1 (=CBSi)

Compound 5d $(C_2H_5O)_2P(O)N(C_6H_5)CH_2CB(C_6H_{11})_2{=}CHSi(CH_3)_3$: Yield = 40%
IR film ν (cm^{-1}): 1595 (C=C), loss of band at 2120 (C≡C)
^1H NMR ($CDCl_3$/TMS) δ (ppm) J (Hz): 0.03 (s, 9H, CH_3), 1.3 (t, 6H, CH_3, J_{H-H} = 5.2), 1.5 (m, 22H, C_6H_{11}), 3.75 (d, 2H, N—CH_2, J_{P-H} = 7.7), 4.0 (q.d, 4H, O—CH_2, J_{P-H} = 7.7, J_{H-H} = 5.2), 5.1 (s, 1H, CH=), 7.2 (m, 5H, C_6H_5)
^{31}P NMR ($CDCl_3/H_3PO_4$) δ (ppm): 4.7
^{13}C NMR ($CDCl_3$) δ (ppm): 0.3 (CH_3—Si), 15.9 (CH_3—CH_2—O), 26.9–27.7 (CH_2 of C_6H_{11}), 34.8 (CH of C_6H_{11}), 51.5 (N—CH_2), 61.5 (O—CH_2), 126.1 (=CH—Si), 127–141 (m, C_6H_5), 169.2 (=CB)

Compound 4e $(C_6H_5O)_2P(O)N(CH_3)CH_2CH{=}CSi(CH_3)_3B(C_6H_{11})_2$: Yield = 70%
IR film ν (cm^{-1}): 1595 (C=C), loss of band at 2120 (C≡C)
^1H NMR ($CDCl_3$/TMS) δ (ppm) J (Hz): 0.09 (s, 9H, CH_3), 1.5 (m, 22H, C_6H_{11}), 2.7 (d, 3H, N—CH_3, J_{P-H} = 9.1), 3.8 (d.d, 2H, N—CH_2, J_{P-H} = 7.5, J_{H-H} = 5.1), 5.4 (t, 1H, CH=, J_{H-H} = 5.3), 7.2 (m, 10H, C_6H_5—O)
^{31}P NMR ($CDCl_3/H_3PO_4$) δ (ppm): 0.91
^{13}C NMR ($CDCl_3$) δ (ppm): 0.9 (CH_3—Si), 26.9–27.7 (CH_2 of C_6H_{11}), 33.1 (N—CH_3), 36.5 (CH of C_6H_{11}), 51.6 (N—CH_2), 120–150 (m, C_6H_5—O), 134.8 (CH=), 156.0 (=CBSi)

Compound 5e $(C_6H_5O)_2P(O)N(CH_3)CH_2CB(C_6H_{11})_2{=}CHSi(CH_3)_3$: Yield = 30%
IR film ν (cm^{-1}): 1595 (C=C), loss of band at 2100 (C≡C)
^1H NMR ($CDCl_3$/TMS) δ (ppm) J (Hz): 0.03 (s, 9H, CH_3), 1.5 (m, 22H, C_6H_{11}), 2.7 (d, 3H, N—CH_3, J_{P-H} = 9.1), 3.7 (d, 2H, N—CH_2, J_{P-H} = 7.7), 5.1 (s, 1H, CH=), 7.2 (m, 10H, C_6H_5)
^{31}P NMR ($CDCl_3/H_3PO_4$) δ (ppm): 0.02
^{13}C NMR ($CDCl_3$) δ (ppm): 0.3 (CH_3—Si), 26.9–27.7 (CH_2 of C_6H_{11}), 33.5 (N—CH_3), 34.8 (CH of C_6H_{11}), 52.6 (N—CH_2), 120–150 (m, C_6H_5), 126.1 (=CH—Si), 169.2 (=CB)

Hydroboration of 2a *with disiamylborane* Sia_2BH

Compound 4l $(C_2H_5O)_2P(O)N(CH_3)CH_2CH{=}CSi(CH_3)_3BSia_2$: Yield = 80%
IR film ν (cm^{-1}): 1590 (C=C), loss of band at 2120 (C≡C)

^{1}H NMR ($CDCl_3$/TMS) δ (ppm) J (Hz): 0.05 (s, 9H, CH_3), 0.90 (m, 18H, CH_3), 1.23 (t, 6H, CH_3, J_{H-H} = 7.02), 2.59 (d, 3H, N—CH_3, J_{P-H} = 9.43), 3.67 (d.d, 2H, N—CH_2, J_{H-H} = 6.31, J_{P-H} = 11.12), 3.9 (q.d, 4H, CH_2—O, J_{H-H} = 7.02, J_{P-H} = 7.02), 5.45 (t, 1H, CH=, J_{H-H} = 6.31)
^{31}P NMR ($CDCl_3$/H_3PO_4) δ (ppm): 9.92

Compound 5l $(C_2H_5O)_2P(O)N(CH_3)CH_2CBSia_2{=}CHSi(CH_3)_3$: Yield = 20%
IR film ν (cm^{-1}): 1590 (C=C), loss of band at 2120 (C≡C)
^{1}H NMR ($CDCl_3$/TMS) δ (ppm) J (Hz): 0.03 (s, 9H, CH_3), 0.90 (m, 18H, CH_3), 1.1 (m, 4H, CH), 1.20 (t, 6H, CH_3, J_{H-H} = 7.02), 2.54 (d, 3H, N—CH_3, J_{P-H} = 9.43), 3.67 (d, 2H, N—CH_2, J_{P-H} = 11.17), 4.7 (q.d, 4H, CH_2—O, J_{H-H} = 7.02, J_{P-H} = 7.02), 5.15 (t, 1H, CH=)
^{31}P NMR ($CDCl_3$/H_3PO_4) δ (ppm): 9.02

General procedure for hydroboration of 2f–i. A freshly prepared solution of borohydride (0.01 mol, 10 ml THF) is added to 0.01 mol of compound 2f–i in 10 ml of THF at 0°C. The reaction is brought to room temperature over 5 min, and is then heated at 40°C for 30 min. The solution is concentrated, and the phosphoramidovinylborane is recovered quantitatively as a non-distillable viscous oil (Table II). The purity as checked by TLC ($CHCl_3$/hexane, 6/1) was adequate for analysis by mass, NMR and IR spectroscopy.[19]

Hydroboration of 2f–i *with dicyclohexylborane* $(Chx)_2BH$

Compound 4f $(C_2H_5O)_2P(O)N(CH_3)CH_2CH{=}CSi(isoC_3H_7)_3B(C_6H_{11})_2$: Yield = 30%
IR film ν (cm^{-1}): 1590 (C=C), loss of band at 2180 (C≡C)
^{1}H NMR ($CDCl_3$/TMS) δ (ppm) J (Hz): 0.9 (d, 18H, CH_3), 1.1 (m, 3H, CH), 1.20 (t, 6H, CH_3, J_{H-H} = 5.2), 1.5 (m, 22H, C_6H_{11}), 2.7 (d, 3H, N—CH_3, J_{P-H} = 8.9), 3.65 (d.d, 2H, N—CH_2, J_{P-H} = 7.7, J_{H-H} = 5.2), 3.9 (q.d, 4H, CH_2—O, J_{P-H} = 7.7, J_{H-H} = 5.2), 5.8 (t, 1H, CH=, J_{H-H} = 5.2)
^{31}P NMR ($CDCl_3$/H_3PO_4) δ (ppm): 9.94
^{13}C NMR ($CDCl_3$) δ (ppm): 12.6 (CH of $isoC_3H_7$), 16.2 (CH_3—CH_2—O), 19.2 (CH_3 of $isoC_3H_7$), 26.9–33.5 (CH_2 of C_6H_{11}), 33.1 (N—CH_3), 36.7 (CH of C_6H_{11}), 51.6 (N—CH_2), 61.9 (O—CH_2), 139.9 (CH=), 152.9 (=CBSi)

Compound 5f $(C_2H_5O)_2P(O)N(CH_3)CH_2CB(C_6H_{11})_2{=}CHSi(isoC_3H_7)_3$: Yield = 70%
IR film ν (cm^{-1}): 1595 (C=C), loss of band at 2180 (C≡C)
^{1}H NMR ($CDCl_3$/TMS) δ (ppm) J (Hz): 1.0 (d, 18H, CH_3), 1.2 (m, 3H, CH—Si), 1.23 (t, 6H, CH_3, J_{H-H} = 5.2), 1.5 (m, 22H, C_6H_{11}), 2.6 (d, 3H, N—CH_3, J_{P-H} = 8.9), 3.7 (d, 2H, N—CH_2, J_{P-H} = 7.7), 4.1 (q.d, 4H, CH_2—O, J_{P-H} = 7.7, J_{H-H} = 5.2), 5.1 (s, 1H, CH=)
^{31}P NMR ($CDCl_3$/H_3PO_4) δ (ppm): 9.22
^{13}C NMR ($CDCl_3$) δ (ppm): 11.6 (CH of $isoC_3H_7$), 18.9 (CH_3 of $isoC_3H_7$), 16.0 (CH_3—CH_2—O), 26.9–33.5 (CH_2 of C_6H_{11}), 33.6 (N—CH_3), 34.8 (CH of C_6H_{11}), 52.6 (N—CH_2), 62.1 (O—CH_2), 121.2 (=CHSi), 169.2 (=CB)

Compound 4g $(C_2H_5O)_2P(O)N(CH_2C_6H_5)CH_2CH{=}CSi(isoC_3H_7)_3B(C_6H_{11})_2$: Yield = 25%
IR film ν (cm^{-1}): 1590 (C=C), loss of band at 2180 (C≡C)
^{1}H NMR ($CDCl_3$/TMS) δ (ppm) J (Hz): 0.9 (d, 18H, CH_3), 1.1 (m, 3H, CH—Si), 1.2 (t, 6H, CH_3, J_{H-H} = 5.2), 3.64 (d.d, 2H, N—CH_2, J_{P-H} = 7.7, J_{H-H} = 5.2), 3.9 (q.d, 4H, CH_2—O, J_{P-H} = 7.7, J_{H-H} = 5.2), 4.1 (d, C_6H_5—CH_2—N, J_{P-H} = 8.5), 5.7 (t, 1H, CH=, J_{H-H} = 5.2), 7.2 (m, 5H, C_6H_5)
^{31}P NMR ($CDCl_3$/H_3PO_4) δ (ppm): 9.72
^{13}C NMR ($CDCl_3$) δ (ppm): 12.6 (CH of $isoC_3H_7$), 19.2 (CH_3 of $isoC_3H_7$), 16.2 (CH_3—CH_2—O), 26.9–33.5 (CH_2 of C_6H_{11}), 36.7 (CH of C_6H_{11}), 41.1 (N—CH_2—C_6H_5), 51.6 (N—CH_2), 61.9 (O—CH_2), 127–141 (m, C_6H_5), 139 (CH=), 152.9 (=CBSi)

Compound 5g $(C_2H_5O)_2P(O)N(CH_2C_6H_5)CH_2CB(C_6H_{11})_2{=}CHSi(isoC_3H_7)_3$: Yield = 75%
IR film ν (cm^{-1}): 1590 (C=C), loss of band at 2180 (C≡C)
^{1}H NMR ($CDCl_3$/TMS) δ (ppm) J (Hz): 1.0 (d, 18H, CH_3), 1.2 (m, 3H, CH—Si), 1.22 (t, 6H, CH_3, J_{H-H} = 5.2), 1.5 (m, 22H, C_6H_{11}), 3.7 (d, 2H, N—CH_2, J_{P-H} = 7.7), 4.0 (q.d, 4H, CH_2—O, J_{P-H} = 7.7, J_{H-H} = 5.2), 4.2 (d, C_6H_5—CH_2—N, J_{P-H} = 8.6), 5.1 (s, 1H, CH=), 7.2 (m, 5H, C_6H_5)
^{31}P NMR ($CDCl_3$/H_3PO_4) δ (ppm): 8.85
^{13}C NMR ($CDCl_3$) δ (ppm): 11.6 (CH of $isoC_3H_7$), 18.9 (CH_3 of $isoC_3H_7$), 16.0 (CH_3—CH_2—O), 26.9–33.5 (CH_2 of C_6H_{11}), 34.8 (CH of C_6H_{11}), 41.1 (N—CH_2—C_6H_5), 52.6 (N—CH_2), 62.1 (O—CH_2), 121.2 (=CHSi), 127–141 (m, C_6H_5), 169.2 (=CB)

Compound 4h $(C_2H_5O)_2P(O)N(C_6H_5)CH_2CH{=}CSi(isoC_3H_7)_3B(C_6H_{11})_2$: Yield = 20%
IR film ν (cm^{-1}): 1590 (C=C), loss of band at 2180 (C≡C)
^{1}H NMR ($CDCl_3$/TMS) δ (ppm) J (Hz): 0.9 (d, 18H, CH_3), 1.1 (m, 3H, CH—Si), 1.23 (t, 6H, CH_3, J_{H-H} = 5.2), 1.5 (m, 22H, C_6H_{11}), 3.6 (d.d, 2H, N—CH_2, J_{P-H} = 7.7, J_{H-H} = 5.2), 3.9 (q.d, 4H,

CH_2—O, J_{P-H} = 7.7, J_{H-H} = 5.2), 5.75 (t, 1H, CH=, J_{H-H} = 5.2), 7.1 (m, 5H, C_6H_5)
^{31}P NMR ($CDCl_3/H_3PO_4$) δ (ppm): 5.5
^{13}C NMR ($CDCl_3$) δ (ppm): 12.6 (CH of $isoC_3H_7$), 19.2 (CH_3 of $isoC_3H_7$), 16.2 (CH_3—CH_2—O), 26.9–33.5 (CH_2 of C_6H_{11}), 36.7 (CH of C_6H_{11}), 51.6 (N—CH_2), 61.9 (O—CH_2), 127–141 (m, C_6H_5), 139.9 (CH=), 152.9 (=CBSi)

Compound 5h $(C_2H_5O)_2P(O)N(C_6H_5)CH_2CB(C_6H_{11})_2$=CHSi$(isoC_3H_7)_3$: Yield = 80%
IR film ν (cm^{-1}): 1590 (C=C), loss of band at 2180 (C≡C)
^1H NMR ($CDCl_3$/TMS) δ (ppm) J (Hz): 1.0 (d, 18H, CH_3), 1.2 (m, 3H, CH—Si), 1.22 (t, 6H, CH_3, J_{H-H} = 5.2), 1.5 (m, 22H, C_6H_{11}), 3.75 (d, 2H, N—CH_2, J_{P-H} = 7.7), 4.1 (q.d, 4H, CH_2—O, J_{P-H} = 7.7, J_{H-H} = 5.2), 5.1 (s, 1H, CH=), 7.2 (m, 5H, C_6H_5)
^{31}P NMR ($CDCl_3/H_3PO_4$) δ (ppm): 4.9
^{13}C NMR ($CDCl_3$) δ (ppm): 11.6 (CH of $isoC_3H_7$), 18.9 (CH_3 of $isoC_3H_7$), 16.0 (CH_3—CH_2—O), 26.9–33.5 (CH_2 of C_6H_{11}), 34.8 (CH of C_6H_{11}), 52.6 (N—CH_2), 62.1 (O—CH_2), 121.2 (=CHSi), 127–141 (m, C_6H_5, 169.2 (=CB)

Compound 4i $(C_6H_5O)_2P(O)N(CH_3)CH_2CH$=CSi$(isoC_3H_7)_3B(C_6H_{11})_2$: Yield = 40%
IR film ν (cm^{-1}): 1590 (C=C), loss of band at 2180 (C≡C)
^1H NMR ($CDCl_3$/TMS) δ (ppm) J (Hz): 0.9 (d, 18H, CH_3), 1.2 (m, 3H, CH—Si), 1.5 (m, 22H, C_6H_{11}), 2.7 (d, 3H, N—CH_3, J_{P-H} = 8.9), 3.6 (d.d, 2H, N—CH_2, J_{P-H} = 7.5, J_{H-H} = 5.6), 5.7 (t, 1H, CH=, J_{H-H} = 5.6), 7.1 (m, 10H, C_6H_5)
^{31}P NMR ($CDCl_3/H_3PO_4$) δ (ppm): 0.8
^{13}C NMR ($CDCl_3$) δ (ppm): 12.6 (CH of $isoC_3H_7$), 19.2 (CH_3 of $isoC_3H_7$), 26.9–33.5 (CH_2 of C_6H_{11}), 33.1 (N—CH_3), 36.7 (CH of C_6H_{11}), 51.6 (N—CH_2), 120–150 (m, C_6H_5), 139.9 (CH=), 152.9 (=CBSi)

Compound 5i $(C_6H_5O)_2P(O)N(CH_3)CH_2CB(C_6H_{11})_2$=CHSi$(isoC_3H_7)_3$: Yield = 60%
IR film ν (cm^{-1}): 1595 (C=C), loss of band at 2180 (C=C)
^1H NMR ($CDCl_3$/TMS) δ (ppm) J (Hz): 1.0 (d, 18H, CH_3), 1.2 (m, 3H, CH—Si), 1.5 (m, 22H, C_6H_{11}), 2.7 (d, 3H, N—CH_3, J_{P-H} = 8.8), 3.6 (d.d, 2H, N—CH_2, J_{P-H} = 7.5, J_{H-H} = 5.6), 5.1 (s, 1H, CH=), 7.2 (m, 10H, C_6H_5—O)
^{31}P NMR ($CDCl_3/H_3PO_4$) δ (ppm): −0.21
^{13}C NMR ($CDCl_3$) δ (ppm): 11.6 (CH of $isoC_3H_7$), 18.9 (CH_3 of $isoC_3H_7$), 26.9–33.5 (CH_2 of C_6H_{11}), 33.6 (N—CH_3), 34.8 (CH of C_6H_{11}), 52.6 (N—CH_2), 120–150 (m, C_6H_5), 121.2 (=CH—Si), 169.2 (=CB)

Hydroboration of 2f with dithexylborane $(Thx)_2BX$

Compound 4r $(C_2H_5O)_2P(O)N(CH_3)CH_2CH$=CSi$(isoC_3H_7)_3B(Thx)_2$: Yield = 90%
IR film ν (cm^{-1}): 1590 (C=C), loss of band at 2180 (C≡C)
^1H NMR ($CDCl_3$/TMS) δ (ppm) J (Hz): 1.03 (d, 18H, CH_3), 1.1 (m, 3H, CHSi), 0.90 (d, 12H, CH_3), 1.1 (s, 12H, CH_3), 1.23 (t, 6H, CH_3, J_{H-H} = 7.02), 1.8 (m, 2H, CH), 2.59 (d, 3H, N—CH_3, J_{P-H} = 9.43), 3.67 (d.d, 2H, N—CH_2, J_{H-H} = 6.31, J_{P-H} = 11.12), 3.9 (q.d, 4H, O—CH_2, J_{H-H} = 7.02, J_{P-H} = 7.02), 5.8 (t, 1H, CH=, J_{H-H} = 6.31)
^{31}P NMR ($CDCl_3/H_3PO_4$) δ (ppm): 9.94

Hydroboration of 2f with diisopinocampheylborane lpc_2BH

Compound 4s $(C_2H_5O)_2P(O)N(CH_3)CH_2CH$=CSi$(isoC_3H_7)_3B(lpc)_2$: Yield = 90%
IR film ν (cm^{-1}): 1590 (C=C), loss of band at 2180 (C≡C)
^1H NMR ($CDCl_3$/TMS) δ (ppm) J (Hz): 1.03 (d, 18H, CH_3), 1.1 (m, 3H, CHSi), 1.9 (m, 26H, CH_2, CH, CH_3), 2.59 (d, 3H, N—CH_3, J_{P-H} = 9.43), 3.67 (d.d, 2H, N—CH_2, J_{H-H} = 6.31, J_{P-H} = 11.12), 3.9 (q.d, 4H, O—CH_2, J_{H-H} = 7.02, J_{P-H} = 7.02), 5.8 (t, 1H, CH=, J_{H-H} = 6.31)
^{31}P NMR ($CDCl_3/H_3PO_4$) δ (ppm): 9.94

Oxidation of the phosphoramidovinylboranes 4 and 5

1) *With $NaOH/H_2O_2$: typical procedure.* 7.5 ml of a 3 M solution of sodium hydroxide followed by 7.5 ml of 30% hydrogen peroxide solution are added to 4.56 g (0.01 mol) of the boron intermediate 4a and 5a in 10 ml of THF. The mixture is refluxed for 30 min. After cooling the solution is hydrolyzed with 20 ml of distilled water. The mixture is then extracted with chloroform (3 × 20 ml). The aqueous phase is acidified with 30 ml of 30% hydrochloric acid and then extracted with chloroform (3 × 20 ml). The different organic phases are dried over anhydrous sodium sulfate, evaporated and analyzed individually (Table V).

2) *With sodium perborate: typical procedure.* 10 ml of distilled water followed by a 30 mmol solution of sodium perborate (4.6 g) are added dropwise to a solution of the organoboron derivatives 4a and

5a (4.56 g, 0.01 mol) in 10 ml of THF under an inert atmosphere. The mixture is cooled in a cold water bath to maintain the reaction at room temperature. After stirring for 2 h, the two phases are separated by extraction with chloroform (3 × 20 ml). The aqueous phase is acidified with 30 ml of 30% hydrochloric acid and then extracted with chloroform (3 × 20 ml). The different organic phases are dried over anhydrous sodium sulfate, evaporated and analyzed individually (Table VI).

3) *With H_2O_2-sodium acetate: typical procedure.* 20 ml of a saturated solution of sodium acetate followed by 7.5 ml of 30% hydrogen peroxide are added to a solution of the organoboron derivatives 4a and 5a (4.56 g, 0.01 mol) under an inert atmosphere and at room temperature. The mixture is refluxed in THF for 30 min, and then extracted with chloroform (2 × 20 ml). The aqueous phases are acidified with 30 ml of 30% hydrochloric acid and extracted with chloroform (3 × 20 ml). The different organic phases are dried over anhydrous sodium sulfate, evaporated and analyzed individually (Table VI).

Synthesis of the dialkylphosphoramidopropionic acids 6a–e. They were obtained from the dialkylphosphoramidates 2a–e by hydroboration with dicyclohexylborane $(Chx)_2BH$. Oxidation by $NaOH—H_2O_2$ was carried out as described above. The chloroform phases after extraction in acid medium are dried over anhydrous Na_2SO_4 and then evaporated under vacuum. The residual oil was purified by recrystallization (Table VII). The spectral and physicochemical characteristics of these compounds are in agreement with those given in Reference 13.

Synthesis of the propargylic dialkylphosphoramidates 8a–e. They were obtained from the dialkylphosphoramidates 1a–e by hydroboration with dicyclohexylborane $(Chx)_2BH$. Oxidation by $NaOH—H_2O_2$ was carried out as described above. The chloroform phases after extraction in basic medium are dried over anhydrous Na_2SO_4 and then evaporated under vacuum to afford compounds 8a–e (Table V). They were characterized by comparison with authentic samples prepared according to Reference 10.

Synthesis of 1-triisopropyl 3-dialkylphosphoramido acetone 7a–i. They were obtained from the phosphoramidates 2 by hydroboration with dithexylborane $(Thx)_2BH$. The mixture was then treated with H_2O_2 in sodium acetate (pH 8) as described above. The residual oil after normal work up contained the ketone 7 together with 2,3-dimethyl-2-butanol. The ketone 7 is degraded by heating and is more conveniently purified on an alumina column eluted with ethyl acetate/hexane (3/1).

Ketone 7a: $(C_2H_5O)_2P(O)N(CH_3)CH_2COCH_2Si(CH_3)_3$: Yield = 38%
IR film ν (cm^{-1}): 1715 (C=O); 1230 (P=O)
^1H NMR ($CDCl_3$/TMS) δ (ppm) J (Hz): 0.09 (s, 9H, CH_3), 1.3 (t, 6H, CH_3, J_{H-H} = 7.02), 2.1 (s, 2H, CH_2—Si), 2.54 (d, 3H, N—CH_3, J_{H-H} = 9.42), 3.6 (d, 2H, N—CH_2, J_{H-H} = 10.08), 4.1 (q.d, 4H, CH_2—O, J_{H-H} = 7.02, J_{P-H} = 7.02)
^{13}C NMR ($CDCl_3$/TMS) δ (ppm): 192 (C=O)
^{31}P NMR ($CDCl_3/H_3PO_4$) δ (ppm): 9.32
Anal. for $C_{11}H_{26}NO_4PSi$: % found C 44.65, H 8.90, N 4.68; % calc. C 44.73, H 8.89, N 4.74.

Ketone 7d: $(C_2H_5O)_2P(O)N(C_6H_5)CH_2COCH_2Si(CH_3)_3$: Yield = 45%
IR film ν (cm^{-1}): 1710 (C=O); 1235 (P=O)
^1H NMR ($CDCl_3$/TMS) δ (ppm) J (Hz): 0.09 (s, 9H, CH_3), 1.25 (t, 6H, CH_3, J_{H-H} = 7.05), 2.3 (s, 2H, CH_2—Si), 3.9 (d, 2H, N—CH_2, J_{P-H} = 10.9), 4.1 (q.d, 4H, CH_2—O, J_{H-H} = 7.05, J_{P-H} = 7.02), 7.1 (m, 5H, C_6H_5)
^{13}C NMR ($CDCl_3$/TMS) δ (ppm): 195 (C=O)
^{31}P NMR ($CDCl_3/H_3PO_4$) δ (ppm): 5.3
Anal. for $C_{14}H_{28}NO_4PSi$: % found C 50.61, H 8.53, N 4.19; % calc. C 50.44, H 8.45, N 4.20.

Ketone 7f $(C_2H_5O)_2P(O)N(CH_3)CH_2COCH_2Si(isoC_3H_7)_3$: Yield = 60%
bp (O, O1) = 135°C with decomposition
IR film ν (cm^{-1}): 1715 (C=O); 1232 (P=O)
^1H NMR ($CDCl_3$/TMS) δ (ppm) J (Hz): 0.99 (d, 18H, CH_3), 1.1 (m, 3H, CH—Si, J_{H-H} = 5.25), 1.3 (t, 6H, CH_3, J_{H-H} = 7.01), 2.07 (s, 2H, CH_2—Si), 2.6 (d, 3H, N—CH_3, J_{P-H} = 9.43), 3.9 (d, 2H, N—CH_2, J_{P-H} = 11.15), 4.0 (q.d, 4H, CH_2—O, J_{H-H} = 7.02, J_{P-H} = 7.02)
^{13}C NMR ($CDCl_3$/TMS) δ (ppm): 192 (C=O)
^{31}P NMR ($CDCl_3/H_3PO_4$) δ (ppm): 9.54
Anal. for $C_{17}H_{38}NO_4PSi$: % found C 53.79, H 10.09, N 3.69; % calc. C 53.92, H 9.88, N 3.48.

Ketone 7g $(C_2H_5O)_2P(O)N(CH_2C_6H_5)CH_2COCH_2Si(isoC_3H_7)_3$: Yield = 65%
IR film ν (cm^{-1}): 1715 (C=O); 1248 (P=O)
^1H NMR ($CDCl_3$/TMS) δ (ppm) J (Hz): 0.99 (d, 18H, CH_3), 1.1 (m, 3H, CH—Si), 1.3 (t, 6H, CH_3, J_{H-H} = 7.02, J_{P-H} = 7.05), 2.08 (s, 2H, CH_2—Si), 3.9 (d, 2H, N—CH_2, J_{P-H} = 10.95), 4.0 (q.d, 4H,

CH_2—O, J_{H-H} = 7.02, J_{P-H} = 7.05), 4.2 (d, 2H, N—CH_2, J_{P-H} = 8.19), 7.2 (m, 5H, C_6H_5)
^{13}C NMR ($CDCl_3$/TMS) δ (ppm): 195 (C=O)
^{31}P NMR ($CDCl_3/H_3PO_4$) δ (ppm): 9.1
Anal. for $C_{23}H_{42}NO_4Psi$: % found C 60.88, H 9.09, N. 2.98; % calc. C 60.63, H 9.29, N 3.07.

Ketone 7h: $(C_2H_5O)_2P(O)N(C_6H_5)CH_2COCH_2Si(isoC_3H_7)_3$: Yield = 63%
IR film ν (cm^{-1}): 1715 (C=O); 1235 (P=O)
^1H NMR ($CDCl_3$/TMS) δ (ppm) J (Hz): 0.99 (d, 18H, CH_3), 1.2 (m, 3H, CH—Si), 1.3 (t, 6H, CH_3, J_{H-H} = 7.02), 2.07 (s, 2H, CH_2—Si), 3.9 (d, 2H, N—CH_2, J_{P-H} = 11.16), 4.0 (q.d, 4H, CH_2—O, J_{H-H} = 7.02, J_{P-H} = 7.02), 7.2 (m, 5H, C_6H_5)
^{13}C NMR ($CDCl_3$/TMS) δ (ppm): 195 (C=O)
^{31}P NMR ($CDCl_3/H_3PO_4$) δ (ppm): 5.0
Anal. for $C_{22}H_{40}NO_4PSi$: % found C 59.78, H 9.09, N 3.20; % calc. C 59.82, H 9.13, N 3.18.

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19. Isolation is difficult as the compounds are only stable in solution and under an inert atmosphere. This accounts for the discrepancies in the elemental analyses. The mass spectra of the compounds in solution were in agreement with the proposed structures.