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Azomethine Derivatives. Part VIII.[1] Preparation of Some Diphenylketiminosilanes, and the Use of Diphenylketiminotrimethylsilane to Prepare Diphenylketiminoboranes

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Improved procedures for the preparation of $Ph_2C{:}NSiR_3$ (R = Me, Et, or Ph) from R_3SiCl + $Ph_2C{:}NLi$ are described. $Ph_2C{:}NSiPh_3$ can also be prepared from $Ph_3SiCl + 2Ph_2C{:}NH$. $SiCl_4$ and $4Ph_2C{:}NLi$ give the new compound $(Ph_2C{:}N)_4Si$.

Reactions between $Ph_2C{:}NSiMe_3$ (I) and boron halides, generally in toluene, provide convenient routes to diphenylketiminoboranes. The trihalides BF_3 (as BF_3,OEt_2), BCl_3, and BBr_3 with (I) give diphenylketiminoboron dihalides $Ph_2C{:}NBX_2$. With two molecules of (I) the same trihalides give $Ph_2C{:}NBX_2 + (Ph_2C{:}N)_3B$, apparently through disproportionation of the monohalides $(Ph_2C{:}N)_2BX$, which could not be isolated. BCl_3 with three molecules of (I) gives $(Ph_2C{:}N)_3B$. Similar reactions between (I) and $PhBCl_2$, the catechol derivative $C_6H_4O_2BCl$, Ph_2BCl, and $(mesityl)_2BF$ have been used to prepare two new apparently dimeric ketiminoboranes, $(Ph_2C{:}NBPhCl)_2$ and $(Ph_2C{:}NBO_2C_6H_4)_2$, and three new monomeric ketiminoboranes $(Ph_2C{:}N)_2BPh$, $Ph_2C{:}NBPh_2$, and $Ph_2C{:}NB(mesityl)_2$.

I.r. spectroscopic details of the ketimino-silanes and -boranes are given, and the mass spectrum of $(Ph_2C{:}N)_4Si$ is briefly discussed.

We here describe the use of an iminosilane, $Ph_2C{:}NSiMe_3$ (I), for the preparation of iminoboranes $(Ph_2C{:}N)_nBX_{3-n}$. Ketimino-[1-4] and aldimino-boranes[5-7] had previously been prepared by the methods exemplified by equations (1)—(4). Even when such reactions proceed essentially to completion, however, they do not necessarily represent convenient routes to particular iminoboranes, as the reaction conditions may require careful control[3] or difficulty may be experienced in separating the products of reactions of type (1)[1] or (3).[4] It appeared that reactions between diphenylketiminotrimethylsilane and boron halides $R_{3-n}BX_n$ ($n = 1, 2$, or 3; equation 5) might provide a useful alternative route to diphenylketiminoboranes, by analogy with the established route (6) to aminoboranes using aminosilanes.[8]

$$Ph_2C{:}NLi + BX_3 \longrightarrow LiX + \frac{1}{n}(Ph_2C{:}NBX_2)_n \qquad (1)^{1,2}$$

$$Ph_2C{:}NH + Me_3B \longrightarrow MeH + \tfrac{1}{2}(Ph_2C{:}NBMe_2)_2 \qquad (2)^{3}$$

$$6Ph_2C{:}NH + BCl_3 \longrightarrow 3Ph_2C{:}NH_2Cl + (Ph_2C{:}N)_3B \qquad (3)^{4}$$

$$2MeC{\vdots}N + Me_4B_2H_2 \longrightarrow (MeCH{:}NBMe_2)_2 \qquad (4)^{5}$$

$$nPh_2C{:}NSiMe_3 + R_{3-n}BX_n \longrightarrow nMe_3SiX + (Ph_2C{:}N)_nBR_{3-n} \qquad (5)$$

$$nMe_3SiNR^1{}_2 + R^2{}_{3-n}BX_n \longrightarrow nMe_3SiX + (R^1{}_2N)_nBR^2{}_{3-n} \qquad (6)$$

Ketiminosilanes were already known to result from reactions between non-enolizable ketones and sodium bis(triorganosilyl)amide in refluxing benzene (7).[9] We chose to use the reaction (8) between diphenylketiminolithium and the appropriate silicon halide, the method

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[1] Part VII, J. R. Jennings, I. Pattison, and K. Wade, *J. Chem. Soc. (A)*, 1969, 565.

[2] I. Pattison, K. Wade, and B. K. Wyatt, *J. Chem. Soc. (A)*, 1968, 837.

[3] I. Pattison and K. Wade, *J. Chem. Soc. (A)*, 1967, 1098.

[4] I. Pattison and K. Wade, *J. Chem. Soc. (A)*, 1968, 842.

[5] J. E. Lloyd and K. Wade, *J. Chem. Soc. (A)*, 1964, 1649.

[6] M. F. Hawthorne, *Tetrahedron*, 1962, **17**, 117.

[7] V. A. Dorokhov and M. F. Lappert, *Chem. Comm.*, 1968, 249.

[8] O. J. Scherer, *Organometallic Chem. Rev.*, 1968, **3**, 281.

[9] C. Krüger, E. G. Rochow, and U. Wannagat, *Chem. Ber.*, 1963, **96**, 2132.

$$R^1_2CO + NaN(SiR^2_3)_2 \longrightarrow R^1_2C{:}NSiR^2_3 + NaOSiR^2_3 \quad (7)$$

$$n Ph_2C{:}NLi + R_{4-n}SiX_n \longrightarrow nLiX + (Ph_2C{:}N)_nSiR_{4-n} \quad (8)$$

recently used by Chan and Rochow to prepare a large number of ketiminosilanes.[10] Our yields based on the chlorosilane were significantly higher than those quoted by Chan and Rochow for the preparation of $Ph_2C{:}NSiMe_3$, $Ph_2C{:}NSiEt_3$, and $Ph_2C{:}NSiPh_3$, and we were able to prepare tetrakis(diphenylketimino)silane, $(Ph_2C{:}N)_4Si$, a compound Chan and Rochow were unable to prepare, from $4Ph_2C{:}NLi + SiCl_4$ in ether at 20°. Our procedure for the preparation of $Ph_2C{:}NSiMe_3$ is given in the Experimental section. The conditions used for the preparation of this and the other diphenylketiminosilanes are summarised in Table 1; analyses are in Table 2. The temperature needed to effect complete reaction between $Ph_2C{:}NLi$ and R_3SiCl increased in the sequence $R = Me < Et < Ph$, so that in the case of $R = Ph$ it was found necessary to pump off most of the ether and add toluene, which was then heated to boiling. The reaction between Ph_3SiCl and an excess of $Ph_2C{:}NH$ in boiling toluene (equation 9; *cf.* equation 3) was found to be an alternative route to $Ph_2C{:}NSiPh_3$, although much slower than that between $Ph_2C{:}NLi$ and Ph_3SiCl. An attempt to prepare $Ph_2C{:}NSiMe_3$ by a similar reaction between $2Ph_2C{:}NH$ and Me_3SiCl failed, apparently because Me_3SiCl distilled out of the solution at the temperature needed for reaction.

TABLE 1

Conditions used to prepare diphenylketimino-derivatives of silicon

Reactants	Solvent, temp., and time	Silicon-containing product (% yield)	Appearance	M.p./b.p.
$Ph_2C{:}NLi$ $+Me_3SiCl$	Et_2O 20°; 30 min.	$Ph_2C{:}NSiMe_3$ 95%	Yellow liquid	92—94° at 10^{-2} mm.
$Ph_2C{:}NLi$ $+Et_3SiCl$	Et_2O 35°; 30 min.	$Ph_2C{:}NSiEt_3$ 85%	Yellow liquid	117—118° at 10^{-2} mm.
$Ph_2C{:}NLi$ $+Ph_3SiCl$	Toluene 96°; 15 min.	$Ph_2C{:}NSiPh_3$ 77%	Yellow crystals [a]	124—125°
$2Ph_2C{:}NH$ $+Ph_3SiCl$	Toluene 96°; 15 hr.	$Ph_2C{:}NSiPh_3$ 42%	,,	,,
$4Ph_2C{:}NLi$ $+SiCl_4$	Et_2O 20°; 1 hr.	$(Ph_2C{:}N)_4Si$ 65%	Large yellow crystals [b]	132—133°

[a] From light petroleum, b.p. 80—100°. [b] From hexane.

$$2Ph_2C{:}NH + Ph_3SiCl \longrightarrow Ph_2C{:}NH_2Cl + Ph_2C{:}NSiPh_3 \quad (9)$$

The i.r. spectra of the diphenylketiminosilanes were recorded; certain differences in band frequencies from those reported by Rochow and his co-workers [9,10] were noted, particularly in the values of ν(C=N). Because of these discrepancies, and because only selected frequencies were reported by Rochow and his co-workers, the frequencies and intensities of all bands in our spectra from 2000 to 500 or 450 cm.$^{-1}$ are listed at the end of the Experimental section.

The mass spectrum of tetrakis(diphenylketimino)silane, $(Ph_2C{:}N)_4Si$, was recorded. Mass and intensity values for the main peaks are in Table 3, together with suggested assignments. Peaks due to fragments containing silicon were readily identified by their characteristic isotope pattern arising from the natural abundances of ^{28}Si (92·3%), ^{29}Si (4·7%), and ^{30}Si (3·0%). The breakdown apparently involves sequential cleavage of $Ph_2C{:}N$ groups, occasional loss or acquisition of hydrogen atoms, and some migration of phenyl groups to silicon. A particularly interesting feature is the number and in two cases the relative intensity of peaks arising from doubly charged fragments. For example, the peak at $m/e = 194$ apparently arises from the doubly charged ion $(Ph_2CN)_2Si^{2+}$ for which a cumulene-type

TABLE 2

Analyses

Compound		C (%)	H (%)	N (%)	Mol. wt.
$Ph_2C{:}NSiMe_3$	Found	75·8	7·3		
	Calc.	75·9	7·6		
$Ph_2C{:}NSiEt_3$	Found	77·1	8·4		
	Calc.	77·3	8·5		
$Ph_2C{:}NSiPh_3$	Found	84·3	5·5		
	Calc.	84·7	5·7		
$(Ph_2C{:}N)_4Si$	Found	83·0	5·3	7·2	723
	Reqd.	83·4	5·4	7·3	748
$(Ph_2C{:}NBPhCl)_n$ † ...	Found	75·2	5·2	4·7	
	Reqd.	75·3	5·0	4·6	
$(Ph_2C{:}N)_2BPh$	Found	85·1	5·6	6·0	441
	Reqd.	85·7	5·6	6·3	448
$Ph_2C{:}NBPh_2$	Found	86·8	5·9	4·2	331
	Reqd.	87·0	5·8	4·1	345
$Ph_2C{:}NB(mesityl)_2$...	Found	86·2	7·8	3·2	443
	Reqd.	86·7	7·5	3·3	429
$(Ph_2C{:}NBO_2C_6H_4)_n$ †	Found	75·5	5·1	4·8	
	Reqd.	76·3	4·7	4·7	

† Not soluble enough in benzene for cryoscopic determination of *n*; mass spectrum indicates *n* probably = 2.

TABLE 3

Mass spectroscopic results for $(Ph_2C{:}N)_4Si$

m/e	Relative intensity	Assignment
748	12	$(Ph_2CN)_4Si$
645	1	$(Ph_2CN)_3SiPh$
568	30	$(Ph_2CN)_3Si$
465	4	$(Ph_2CN)_2SiPh$
388	2	$(Ph_2CN)_2Si$
387	4	388 minus H
374	0·1	$(Ph_2CN)_4Si$ †
285	4	$Ph_2CNSiPh$
284	13	$Ph_2CNSiPh$ minus H
259	10	Ph_3Si
245·5	0·1	$(Ph_2CN)_3Si$ minus Ph †
232·5	0·1	$(Ph_2CN)_2SiPh$ †
208	1	Ph_2CNSi
194	6	$(Ph_2CN)_2Si$ †
182	7	Ph_2Si
181	60	Ph_2CNH
180	100	Ph_2CN
142·5	8	$Ph_2CNSiPh$ †
105	9	PhSi
104	50	PhCNH
90	5	PhCH
78	27	PhH
77	38	Ph

† Doubly charged ions.

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[10] L.-H. Chan and E. G. Rochow, *J. Organometallic Chem.*, 1967, **9**, 231.

structure $[Ph_2C{:}N{:}Si{:}NCPh_2]^{2+}$ appears possible [*cf.* the relative abundance of $(Ph_2C{:}N)_2B^+$, which could be written $Ph_2C{:}N{:}B{:}N{:}CPh_2{}^+$, in the mass spectrum[1] of $(Ph_2C{:}NBF_2)_n$].

The conditions found suitable for the preparation of diphenylketiminoboranes from $Ph_2C{:}NSiMe_3$ and various boron halides in toluene are summarised in Table 4. Analyses for the new boron compounds so prepared are in Table 2.

TABLE 4

Conditions used to prepare diphenylketimino-derivatives of boron from $Ph_2C{:}NSiMe_3$ (I) + boron halides in toluene

Reactants	Maximum temp. and time [a]	Boron-containing product(s)	Appearance	M.p.
(I) + BX_3 [b]	20°; ½—1 hr.	$(Ph_2C{:}NBX_2)_n$	[c]	[c]
2(I) + BX_3 [b]	96°; 15—30 min.	$(Ph_2C{:}NBX_2)_n$	[c]	[c]
		+ $(Ph_2C{:}N)_3B$	Wax [d]	
3(I) + BCl_3	96°; 30 min.	$(Ph_2C{:}N)_3B$	Wax [d]	
(I) + $PhBCl_2$	96°; 15 min.	$(Ph_2C{:}NBPhCl)_n$	Colourless needles [d]	237—238°
2(I) + $PhBCl_2$	96°; 2 hr.	$(Ph_2C{:}N)_2BPh$	Colourless needles [e]	127—128
(I) + Ph_2BCl	96°; 2 hr.	$Ph_2C{:}NBPh_2$	Colourless crystals [e]	143—144
(I) + mesityl$_2$BF	150°; 16 hr.	$Ph_2C{:}NB(mesityl)_2$	Colourless crystals [e]	168—170
(I) + $C_6H_4O_2BCl$ (VIII)	20°; 30 min.	$(Ph_2C{:}NBO_2C_6H_4)_n$	Golden needles [d]	210—212

[a] The conditions given in this column indicate the time for which the mixture was held at the maximum temperature used to ensure reaction. In many cases reaction actually occurred below room temperature (see text). [b] X = F, Cl, or Br; when X = F, the ether complex BF_3,OEt_2 was used. [c] Varies according to X; see ref. 1. [d] From toluene. [e] From light petroleum, b.p, 80—100°. [f] No solvent.

In the reactions involving boron trihalides, equimolar proportions of BX_3 and $Ph_2C{:}NSiMe_3$ were mixed in toluene at —78°. Reaction (10) apparently occurred as the mixture warmed to about 0°, as shown by the

$$Ph_2C{:}NSiMe_3 + BX_3 \longrightarrow Me_3SiX + \frac{1}{n}(Ph_2C{:}NBX_2)_n \qquad (10)$$

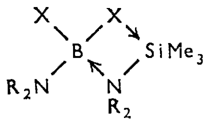
deposition of solid $(Ph_2C{:}NBX_2)_n$, identified by comparison of its m.p. and i.r. spectrum with samples prepared from $(Ph_2C{:}N)_3B + BF_3$, or from $Ph_2C{:}NLi + BX_3$.[1] Reaction (10) thus affords probably the best route to $(Ph_2C{:}NBF_2)_n$, and a more convenient route to the other dihalides than does the ketiminolithium route,[1] which involves tedious separations from lithium halide of the slightly toluene-soluble chloride $(Ph_2C{:}NBCl_2)_2$ and bromide $(Ph_2C{:}NBBr_2)_2$.

When the boron trihalides were treated with 2 mol. of $Ph_2C{:}NSiMe_3$ in toluene at —78° in attempts at reaction (11) the products obtained in each case were

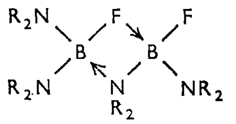
$$BX_3 + 2Ph_2C{:}NSiMe_3 \longrightarrow 2Me_3SiX + (Ph_2C{:}N)_2BX \qquad (11)$$

$(Ph_2C{:}NBX_2)_n$ (as a precipitate, which separated at about 0°) and $(Ph_2C{:}N)_3B$. It appears that bis(diphenylketimino)boron halides are unstable with respect to disproportionation into $Ph_2C{:}NBX_2$ and $(Ph_2C{:}N)_3B$ (equation 12), and that the products isolated from these reactions reflect the low solubility of the dihalides $(Ph_2C{:}NBX_2)_n$ which are precipitated from solution, thereby displacing equilibrium (12) to the right. As the low solubility of the dihalides and the co-ordinative saturation of the boron atoms makes them slow to react further with $Ph_2C{:}NSiMe_3$ in toluene, it appears that formation of $(Ph_2C{:}N)_2BX$, and its disproportionation into $(Ph_2C{:}NBX_2)_n$ and $(Ph_2C{:}N)_3B$, proceeds in solution at the low temperature (*ca.* 0°) at which $(Ph_2C{:}NBX_2)_n$ slowly separates as a precipitate, rather than that solid $(Ph_2C{:}NBX_2)_n$ reacts further with $Ph_2C{:}NSiMe_3$. In this respect an interesting comparison can be drawn with the behaviour of aminoboranes. The formation of aminoboranes from aminosilanes,[11] and redistribution (disproportionation) reactions of aminoboranes,[12,13] are believed to involve intermediate complexes of types (II) and (III) respectively. When the amino-groups R_2N are bulky, (II) and (III) can form less readily, and the bisaminoboranes are more difficult to prepare by this route, though less liable to disproportionate once prepared.[12,14] In the case of our iminoboranes, the shape of the imino-group $Ph_2C{:}N$ possibly allows readier access to the nitrogen for the formation of analogous intermediates (IV) and (V).

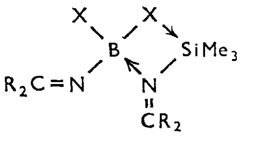
$$2(Ph_2C{:}N)_2BX \rightleftharpoons \frac{1}{n}(Ph_2C{:}NBX_2)_n + (Ph_2C{:}N)_3B \qquad (12)$$



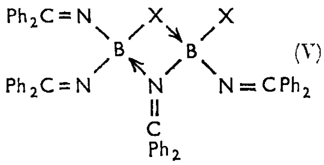
(II)



(III)



(IV)



(V)

A further indication that an excess of $Ph_2C{:}NSiMe_3$ will rapidly replace more than one halogen of BX_3 below

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[11] H. Nöth, *Z. Naturforsch.*, 1961, **16b**, 618.

[12] H. Nöth and H. Vahrenkamp, *Chem. Ber.*, 1966, **99**, 2757.

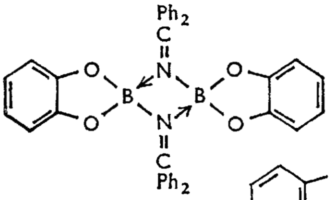
[13] D. W. Aubrey, M. F. Lappert, and M. K. Majumdar, *J. Chem. Soc.*, 1962, 4088.

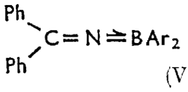
[14] C. R. Russ and A. G. MacDiarmid, *Angew. Chem., Internat. Edn.*, 1964, **3**, 509.

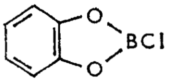
0° in toluene without initial precipitation of $(Ph_2C{:}NBX_2)_n$ was provided by a study of the system BCl_3–$3Ph_2C{:}NSiMe_3$ in toluene. The components were mixed at −78°, the solution was warmed to 20° with stirring, and ultimately heated to boiling for 30 min. At no time did a precipitate separate, and the only boron-containing product obtained was $(Ph_2C{:}N)_3B$.

Rapid transfer of diphenylketimino-groups from silicon to boron was also observed in our studies of the systems $PhBCl_2$–$Ph_2C{:}NSiMe_3$ and $PhBCl_2$–$2Ph_2C{:}NSiMe_3$. When the reactants were mixed at −78° in 1 : 1 molar proportion in toluene and allowed to warm, $(Ph_2C{:}NBPhCl)_n$ was deposited slowly below 0°. With use of 1 : 2 molar proportions, however, the solution remained clear when warmed to 20° and also when heated to 96°, and the only solid product recovered was $(Ph_2C{:}N)_2BPh$. This bis(ketimino)-derivative was stable with respect to disproportionation into $(Ph_2C{:}N)_3B$ and $Ph_2C{:}NBPh_2$, despite its monomeric state of association. The greater stability to disproportionation of $(Ph_2C{:}N)_2BPh$ than of $(Ph_2C{:}N)_2BX$ (X = F, Cl, or Br) may result from the greater bulk and weaker bridging properties of phenyl groups than halogens, both of which factors would inhibit formation of an intermediate analogous to (V).

In reactions involving diarylboron halides, diphenylboron chloride and diphenylketiminotrimethylsilane apparently reacted to form $Ph_2C{:}NBPh_2$ and Me_3SiCl at about 0—20° in toluene, when the colour due to the silane faded, though the solution was boiled for 2 hr. to ensure completion of reaction. The more sterically hindered dimesitylboron fluoride required 14 hr. at 150° in the absence of solvent to ensure a reasonable extent of reaction with $Ph_2C{:}NSiMe_3$. The benzodioxaborole, $C_6H_4O_2BCl$ (VIII), by contrast, the shape of which allows readier access to the boron, reacted at a much lower temperature. When mixed with $Ph_2C{:}NSiMe_3$ at −78°, it formed a gelatinous red precipitate (possibly an intermediate complex) which dissolved rapidly on warming. At about −50° a yellow precipitate formed. This after recrystallisation was identified as 2-diphenylketimino-1,3,2-benzodioxaborole which, judged by its mass spectrum, is dimeric and so presumed to have structure (VI).


(VI)


(VII)


(VIII)

Of the five new boron compounds described in this paper, three [$(Ph_2C{:}N)_2BPh$, $Ph_2C{:}NBPh_2$, and $Ph_2C{:}NB(mesityl)_2$] were monomeric in benzene. The last two had i.r. absorption bands near 1790 cm.$^{-1}$ which we assign to a stretching vibration, ν(C═N═B), of the apparently linear skeleton of these molecules (VII). The relationship between these compounds and allenes has been noted.[15] Discussion of their properties and spectra will be deferred until a later paper in which a series of monomeric iminoboranes will be described.[16]

EXPERIMENTAL

Materials and Techniques.—Commercial trimethylchlorosilane, triethylchlorosilane, and silicon tetrachloride were distilled before use. Triphenylchlorosilane was prepared from $SiCl_4 + 3PhMgBr$, and had m.p. 94—95° (lit.[17] 96°). Phenylboron dichloride and diphenylboron chloride were prepared from BCl_3 and Ph_4Sn.[18] Dimesitylboron fluoride was prepared from BF_3,OEt_2 and (mesityl)MgBr.[19] 2-Chloro-1,3,2-benzodioxaborole was prepared from catechol and boron trichloride.[20] Manipulations were carried out using a nitrogen-filled glove box or nitrogen-filled apparatus as appropriate.

Spectra.—I.r. spectra were recorded on a Grubb-Parsons prism-grating GS2A spectrometer or Spectromaster. Mass spectra were recorded on an A.E.I. M.S.9 instrument at 70 ev and an accelerating potential of 8 kv, with a source temperature of 150—250° and electromagnetic scanning. Samples were inserted directly into the ion source.

Analyses.—C, H, and N were determined by conventional combustion techniques. Molecular weights were determined cryoscopically in benzene.

Preparation of Diphenylketiminotrimethylsilane.—*n*-Butyllithium (100 mmoles in hexane) was added by syringe to a frozen (−196°) solution of diphenylketimine (18·1 g., 100 mmoles) in ether, and the mixture was allowed to warm to 20° and stirred for 40 min. The bright red solution was then cooled to −196° and trimethylchlorosilane (10·8 g., 100 mmoles) was added by syringe. The red colour changed to yellow as the mixture warmed to 0°, and lithium chloride was precipitated. The solution was stirred for 30 min. and then filtered to remove lithium chloride. The ether was pumped off, leaving a yellow liquid which after distillation at 92—94°/10^{-2} mm., was identified as $Ph_2C{:}NSiMe_3$. Its i.r. spectrum was identical to that reported by Krüger, Rochow, and Wannagat.[9]

The variations on the above procedure used in the preparation of $Ph_2C{:}NSiEt_3$, $Ph_2C{:}NSiPh_3$, and $(Ph_2C{:}N)_4Si$ are indicated in Table 1. Conditions for the reactions between $Ph_2C{:}NSiMe_3$ and boron halides are summarized in Table 4.

I.r. Spectra.—Frequencies and intensities of bands in the i.r. spectra of the new compounds, and of those known compounds whose spectra had not previously been fully reported, were as follows:

$Ph_2C{:}NSiEt_3$ (liquid film): 1666vs, 1605m, 1575m, 1493w, 1453s, 1422m, 1370s, 1316m, 1271s, 1245s, 1199m, 1183m, 1153w, 1076m, 1032m, 1016s, 1004s, 976m, 937s, 908s, 892m, 826vs, 790s, 761m, 737vs, 725vs, 699vs, 678sh, 630m, 624s, 591w, 578w, and 526w cm.$^{-1}$.

$Ph_2C{:}NSiPh_3$ (Nujol mull): 1667s, 1650s, 1600w, 1580w, 1314m, 1267s, 1188w, 1178w, 1153w, 1114s, 1105m, 1075w,

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[15] J. R. Jennings, I. Pattison, C. Summerford, K. Wade, and B. K. Wyatt, *Chem. Comm.*, 1968, 250.

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1029m, 1002w, 937m, 906m, 837s, 780m, 753m, 741m, 720m, 712vs, 690vs, 633m, 547m, 513s, 510vs, 478m, and 453w cm.$^{-1}$.

$(Ph_2C\dot{:}N)_4Si$ (Nujol mull) 1646vs, 1600m, 1580m, 1488w, 1450s, 1316m, 1271s, 1181m, 1163m, 1075m, 1031m, 1003w, 990w, 939s, 930m, 913s, 866s, 848s, 835s, 790s, 761m, 754m, 699vs, 681m, 635s, 623w, 615w, 557sh, 551m, 540m, and 459w cm.$^{-1}$.

$(Ph_2C\dot{:}NBPhCl)_n$ (Nujol mull): 1612m, 1587s, 1565m, 1333m, 1316sh, 1271m, 1200w, 1186s, 1172w, 1111w, 1075w, 1042w, 1028wsh, 1013s, 930s, 917w, 885s, 848m, 833sh, 830m, 789m, 763m, 746w, 706s, 698s, 680m, 672w, 568s, 502w, and 479w cm.$^{-1}$.

$(Ph_2C\dot{:}N)_2BPh$ (Nujol mull): 1672vs, 1598m, 1577w, 1311m, 1266sh, 1250s, 1217s, 1176w, 1159w, 1122s, 1072w, 1058m, 1027w, 1009s, 999m, 990w, 937m, 926m, 908m, 848w, 788m, 767m, 749s, 719w, 699vs, 679sh, 642s, 586sh, and 578m cm.$^{-1}$.

$Ph_2C\dot{:}NBPh_2$ (Nujol mull): 1786vs, 1595m, 1328w, 1316w, 1269s, 1250s, 1235vs, 1179w, 1149m, 1092m, 1074m, 1064m, 1031m, 990w, 970w, 930m, 909m, 894w, 885s, 799br,sh, 787s, 766m, 752m, 726vs, 695vs, 633vs, 606s, and 579vs cm.$^{-1}$.

$Ph_2C\dot{:}NBmesityl_2$ (Nujol mull): 1792vs, 1610s, 1546w, 1449vs, 1429sh, 1376s, 1316m, 1289sh, 1282s, 1256m, 1241w, 1221sh, 1212m, 1182w, 1149m, 1133m, 1085w, 1075w, 1058w, 1030m, 1018sh, 1001w, 980w, 962w, 935s, 914m, 904sh, 882w, 853vs, 840vs, 788vs, 770m, 742m, 708s, 698vs, 667w, 657w, 641s, 633m, 625s, 615m, 583m, 563w, and 560w cm.$^{-1}$.

$Ph_2C\dot{:}NBO_2C_6H_4$ (Nujol mull): 1624s, 1600m, 1570w, 1490vs, 1328m, 1299w, 1266w, 1235s, 1209w, 1174w, 1134w, 1099s, 1087s, 1071s, 1029m, 1004m, 971w, 943s, 923m, 909sh, 867w, 828w, 783w, 735s, 714s, 698sh, 620w, and 576m cm.$^{-1}$.

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