calization. Since the proton coefficients in this MO are so large, it could have a significant effect on the observed contact shift pattern. Unfortunately, the contact shifts of two protons do not provide enough information to answer this question or to distinguish between the relative importance of π and π^* orbitals. The only conclusion that can be drawn is that the ligand is so arranged in the complex that orbitals with π symmetry can overlap the e_g set.

Examination of Table II shows that the ratios of the shifts in Ni(II) and Co(II) complexes are identical and one might incorrectly infer that these data indicate the spin delocalization mechanisms are essentially the same. The similarity is at first glance surprising, since one does not in general expect the mechanisms of delocalization to be the same in six-coordinate[18] cobalt(II) and nickel(II) and one expects pseudocontact contributions for the six-coordinate Co(II) complex. In a previous report[14] from this laboratory, it was demonstrated that, for systems with rapidly exchanging ligands, the pseudocontact shift would be greatly reduced or become zero. The similarity of our cobalt(II) shifts with those obtained in more dilute solution indicates ion pairing is not extensive and rapid exchange with the excess ligand present eliminates contributions to the isotropic shift from pseudocontact effects. Since we are observing contact shifts for cobalt(II), we can ask the question why are the ratios of the proton shifts identical for Co(II) and Ni(II) when Co(II) has unpaired electrons in both e_g and t_{2g} sets (*i.e.*, σ- and π-type orbitals) and nickel(II) only has them in the e_g set. Here we have the interesting case that the nickel–ligand geometry allows the e_g orbitals on the nickel to mix with both σ- and π-type ligand orbitals. Furthermore, since the proton coefficients are so small in the σ MO, the π-delocalization pattern (Table III) dominates the proton shifts in both the cobalt(II) and nickel(II) complexes contrary to what is to be expected generally. If the ligand σ and π molecular orbitals mixed only with the e_g or t_{2g} set, respectively, different proton shifts would have been expected in cobalt(II) and nickel(II). If the e_g orbitals of the metal ion distributed spin differently between the π and σ MO's of the ligand than the t_{2g} set does, we would also have expected different delocalization patterns in nickel(II) and cobalt(II). Again, the small proton coefficients in the σ MO preclude our gaining information about this and ^{13}C shifts would be enlightening.

It is interesting to point out that as a consequence of the small proton coefficients in the σ MO and the ligand geometry we can say after the fact that the ratio method[16] would have worked on this system if it were needed for the cobalt(II) complex. However, the ratios of the 2-H and 4-CH_3 shifts to the 3-H shift in bis(2,4-pentanedionato)bis(4-methylpyridine *N*-oxide)nickel(II), 1.85 and 2.35, and bis(4-methylpyridine *N*-oxide)bis(dipivaloylmethido)nickel(II), 1.88 and 2.47, are significantly different from these same ratios in the hexakis(4-methylpyridine *N*-oxide)nickel(II) perchlorate, 1.28 and 2.07. The shifts for the former two compounds were reported assuming that the systems were in the fast-exchange region.[19] If the reported shifts are correct, then this demonstrates that even though the ligand is coordinated to the same metal ion, the proton delocalization pattern is similar, but not identical in the series of nickel(II) complexes even though the proton pattern is the same in this and in the six-coordinate nickel(II) and cobalt(II) complexes. As has been previously claimed,[20] it is practically impossible to determine *a priori* when the delocalization mechanisms will be the same in different complexes. Very slight differences in coordination geometries can lead to varying participation by different molecular orbitals in the delocalization mechanism. This shortcoming makes the ratio method for factoring out the pseudocontact shift extremely unreliable contrary to a recent claim made for its judicious utility.[21]

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Preparation of a New Ternary Lithium Silicon Nitride, $LiSi_2N_3$, and the High-Pressure Synthesis of Magnesium Silicon Nitride, $MgSiN_2$

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Prior to this study the only known ternary compound of lithium, silicon, and nitrogen was Li_5SiN_3, first prepared by Juza, *et al.*,[2] who also synthesized the compounds Li_5TiN_3 and Li_5GeN_3. These materials were prepared by reaction of the binary nitrides at temperatures of 850–1300° and were reported to be light in color, easily hydrolyzable, and saltlike in their properties.

David and Lang[3] have reported the ambient-pressure synthesis of magnesium silicon nitride, $MgSiN_2$, by the direct reaction of the binary nitrides. Earlier work led to the synthesis of $CaSiN_2$ by Wöhler and Bock[4] and to the preparation of $BeSiN_2$ by Eckerlin, *et al.*[5]

The purpose of this communication is to report the ambient-pressure, high-temperature synthesis of lithium silicon nitride, $LiSi_2N_3$, and the high-pressure, high-temperature synthesis of magnesium silicon nitride, $MgSiN_2$. Powder X-ray diffraction data for these ternary compounds are also reported.

Experimental Section

A. Lithium Silicon Nitride.—$LiSi_2N_3$ was prepared directly

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(2) R. Juza, H. H. Weber, and E. Meyer-Simon, *Z. Anorg. Allg. Chem.*, **273**, 48 (1953).

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from the binary nitrides Li_3N and Si_3N_4. Lithium nitride was prepared in this laboratory after the method of Goubeau and Anselment.[6] Clean elemental lithium (Fisher Scientific Co.) was placed in an iron boat and the latter inserted into an alumina ceramic tube situated in a high-temperature electrically heated tube furnace. After thoroughly flushing the tube with dry, oil-pumped N_2 (Linde Co.), the lithium metal was heated to 600° for 1 hr under an N_2 flow of approximately 200 cm^3/min. After cooling under an N_2 atmosphere, the reaction product in the boat was found to be a hard and brittle, glassy, reddish black solid. The yield of Li_3N was found to be 99.3% of theoretical as determined from an increase in weight of the sample. Identification of the product as Li_3N was confirmed by X-ray diffraction analysis. Silicon nitride powder (Si_3N_4) of 99% purity was obtained from the Mining and Metals Division of the Union Carbide Corp.

Lithium silicon nitride was prepared by heating stoichiometric mixtures of Si_3N_4 and Li_3N powders at 1200–1500° in an iron boat under an N_2 atmosphere in the same apparatus and following the same procedure employed in preparing Li_3N.

X-Ray powder diffraction data were obtained employing a Debye–Scherrer 114.59-mm camera in conjunction with a Norelco X-ray generator with Cu Kα radiation. The density of $LiSi_2N_3$ was determined by the pycnometric method using toluene as the displaced fluid.

B. Magnesium Silicon Nitride.—$MgSiN_2$ was prepared directly from the binary nitrides Mg_3N_2 and Si_3N_4. Magnesium nitride was prepared in this laboratory after the method of Mitchell.[7] Chemically pure Mg metal turnings (Fisher Scientific Co.) were placed in a stainless steel boat and heated in the same tube furnace used to prepare Li_3N. After thoroughly flushing the tube with dry, oil-pumped N_2 (Linde Co.), the Mg metal was heated for 3 hr at 700° followed by 16 hr at 940° under an N_2 flow of approximately 200 cm^3/min. After cooling under an N_2 atmosphere, a light yellow powder was removed from the steel boat. X-Ray diffraction analysis of the product showed only single-phase Mg_3N_2 to be present. High-pressure, high-temperature synthesis experiments were performed in a single-staged piston–cylinder high-pressure apparatus similar to that described by Boyd and England.[8] Pressure calibration of the apparatus up to 50 kbars was performed by the conventional measurement of electrical resistance changes in bismuth ($Bi(I) \rightleftharpoons Bi(II) \rightleftharpoons Bi(III)$ transitions) and thallium ($Tl(II) \rightleftharpoons Tl(III)$ transition) as a function of ram load. Bismuth and thallium metal wires were enclosed in AgCl sleeves which were situated in the high-pressure sample chamber. Calibration points for the bismuth and thallium transition pressures have been published by Kennedy and LaMori.[9] Temperature–power calibration measurements were made up to approximately 1200° by chromel–alumel thermocouples. Precompressed pellets of thoroughly mixed Mg_3N_2 and Si_3N_4 powders were placed in a boron nitride capsule which in turn was fitted inside a cylindrical graphite furnace. Details of the high-pressure furnace assembly are given in the Boyd and England article.[8] Samples were subjected to pressures ranging from 10 to 30 kbars and temperatures from 800 to 1400°, temperatures over 1200° being read from an extrapolation of the temperature–power calibration curve. Reaction times were on the order of 5 min. High-pressure products were evaluated by means of standard X-ray powder diffraction techniques.

Results and Discussion

The new lithium silicon nitride binary compound synthesized during the course of this work was analyzed chemically. *Anal.* Calcd for $LiSi_2N_3$: Li, 6.60; N, 39.97; Si, 53.43. Found: Li, 6.98; N, 38.2; Si, 51.2. The density of $LiSi_2N_3$ was found to be 2.92 g cm^{-3}.

A hexagonal unit cell for $LiSi_2N_3$ was found by using the graphical method described by Bunn.[10] A least-squares refinement of the observed d spacings yielded the unit cell parameters $a = 6.578 \pm 0.004$ Å and $c = 13.791 \pm 0.020$ Å. A value of 9 $LiSi_2N_3$ formula weights per unit cell was calculated. Error limits are estimated to be ±5%. In Table I are given observed and calculated d spacings and observed line intensities for $LiSi_2N_3$.

TABLE I
X-RAY POWDER DIFFRACTION DATA ON $LiSi_2N_3$

Miller indices				Interplanar spacings, d, Å	
h	k	l	Intens	Calcd	Found
0	0	3	100	4.597	4.595
1	1	0	100	3.289	3.300
2	0	2	100	2.632	2.650
1	1	4	80	2.380	2.384
0	0	6	80	2.294	2.316
2	1	1	10	2.127	2.113
2	1	2	5	2.055	2.065
2	0	6	50	1.789	1.773
0	0	8	20	1.724	1.736
2	0	7	20	1.621	1.631
0	0	9	50	1.532	1.530
3	1	3	5	1.494	1.502
2	2	5	5	1.412	1.403
3	0	7	40	1.367	1.363
4	0	4	5	1.316	1.326
3	2	0	5	1.307	1.307
3	2	2	30	1.284	1.288
3	0	8	10	1.276	1.275
3	1	7	5	1.233	1.231
1	1	11	5	1.172	1.172
1	2	10	5	1.161	1.160
3	3	5	10	1.019	1.018
3	1	11	10	0.9820	0.9812
6	0	1	5	0.9471	0.9474
6	0	5	5	0.8977	0.8984
5	2	6	5	0.8478	0.8472
6	1	5	5	0.8285	0.8285

Synthesis of the ternary lithium silicon nitrides Li_5SiN_3 or $LiSi_2N_3$ depends upon the mole ratio of Li_3N to Si_3N_4 in the starting material as shown in the equations

$$5Li_3N + Si_3N_4 \longrightarrow 3Li_5SiN_3 \quad (1)$$

$$Li_3N + 2Si_3N_4 \longrightarrow 3LiSi_2N_3 \quad (2)$$

The only product resulting from the high-pressure, high-temperature reaction of Mg_3N_2 and Si_3N_4 was found to be magnesium silicon nitride. *Anal.* Calcd for $MgSiN_2$: Mg, 30.2; N, 34.8; Si, 34.9. Found: Mg, 29.9; N, 32.8; Si, 34.1. The reaction between Mg_3N_2 and Si_3N_4 is

$$Mg_3N_2 + Si_3N_4 \longrightarrow 3MgSiN_2 \quad (3)$$

The observed d spacings and line intensities for $MgSiN_2$ are given in Table II along with David and Lang's[3] data for comparison.

In general, the agreement between the X-ray powder diffraction data on $MgSiN_2$ obtained in this study and those given by David and Lang is good. It is of interest to note that two fairly strong lines, at 3.33 and 1.224 Å, observed in this study were not observed by David and Lang.

Conclusions

Lithium silicon nitride, $LiSi_2N_3$, was prepared by the direct reaction between Li_3N and Si_3N_4 at 1200–1500° in an N_2 atmosphere. X-Ray powder diffraction data on $LiSi_2N_3$ were also obtained. Magnesium silicon nitride was prepared by the direct reaction of Mg_3N_2 and Si_3N_4 at 1000–1400° at pressures from 10 to 30 kbars in a piston–cylinder apparatus. X-Ray powder

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TABLE II
X-RAY POWDER DIFFRACTION DATA ON $MgSiN_2$

This work		David and Lang[3]	
Interplanar spacing, d, Å	Intens	Interplanar spacing, d, Å	Intens
4.07	14	4.08	Minor
3.94	15	3.94	Minor
3.33	17		
2.76	79	2.75	Very strong
2.63	55	2.65	Strong
2.49	86	2.49	Very strong
2.41	100	2.41	Very strong
2.33	29	2.33	Moderate
2.19	5		
2.105	6		
1.85	25	1.85	Moderate
1.81	13	1.81	Trace
1.615	20	1.614	Minor
1.576	26	1.543	Moderate
		1.404	Faint
1.377	6	1.379	Faint
1.356	13	1.356	Trace
1.328	9	1.329	Faint
1.312	17	1.312	Minor
		1.275	Very faint
1.247	5	1.246	Very faint
1.224	24		
1.207	8	1.207	Very faint
1.069	6		
1.061	23		
1.033	17		
1.001	15		
0.987	5		
0.984	5		
0.972	6		
0.970	12		
0.938	10		
0.931	9		
0.919	8		
0.892	9		
0.871	14		
0.862	13		
0.858	6		
0.829	7		
0.808	13		
0.796	7		

diffraction data on $MgSiN_2$ powder were obtained and compared with previously published results.

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Some Ring Expansion Reactions of Phosphorus and Boron Imidazolidines (1,3-Diaza-2-phospholidines and -borolidines)

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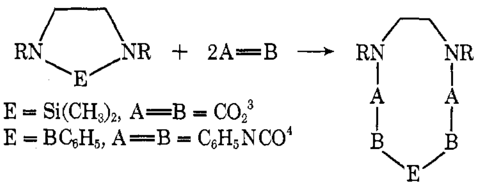
Insertion reactions are especially significant in organometallic chemistry in providing easy syntheses of compounds containing functional groups.[2] Insertion of unsaturated substrates into the E–N bonds of silicon[3] and boron imidazolidines[4] has led to nine-membered, ring-expanded products



$E = Si(CH_3)_2$, $A{=}B = CO_2$[3]
$E = BC_6H_5$, $A{=}B = C_6H_5NCO$[4]

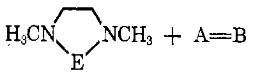
(1)

This paper reports several examples of the insertion reactions of boron and phosphorus imidazolidines.

Results and Discussion

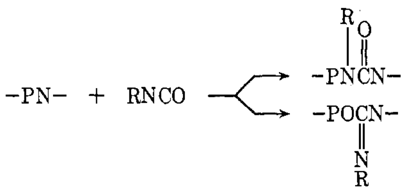
The reaction of methyl and phenyl isocyanates with 1,3-dimethyl-2-phenyl-1,3-diaza-2-phospholidine (phosphorus imidazolidine) on a millimole scale in benzene is exothermic and gives in each case a material containing 2 mol of the isocyanate with a strong absorption at *ca.* 1700 cm^{-1} in the infrared region which could be due to either the C═O or C═N groups, depending on the mode of insertion (see Table I).

TABLE I
DATA FOR



			Anal.,[a] %			
			Calcd		Found	
A═B	Ratio	Form	C	H	C	H
		$E = PC_6H_5$				
CH_3NCO	1:2	Light yellow, low melting	54.53	6.82[b]	52.77	6.82[b]
C_6H_5NCO	1:2	Dark yellow oil	66.67	5.77	65.63	6.03
Cl_3CCHO	1:1	Brown oil	42.15	4.68	42.79	4.52
CS_2	1:1	Red solid, mp 88–99°	48.89	5.65	50.69	6.22
		$E = BC_6H_5$				
Cl_3CCHO	1:2	Brown solid, mp 74–75°	35.95	3.52	36.88	3.98
C_6H_5NCS	1:1	White solid, mp 63–64°	66.00	6.51	66.05	6.57

[a] Microanalyses were performed by Instranal Laboratory, Inc., Rensselaer, N. Y. [b] N: calcd, 18.18%; found, 18.3%.



(2)

By analogy with the findings of Lappert, *et al.*,[5] and Hudson, *et al.*,[6] we assume that the insertion of N═C had taken place to yield a nine-membered bis(ureido)-phenylphosphine ring as depicted in eq 1. The reaction of phenyl isocyanate with boron imidazolidine gives the analogous bis(ureido)borane.[4]

1,3-Dimethyl-2-phenyl-1,3-diaza-2-borolidine (boron imidazolidine) reacts with phenyl isothiocyanate to form

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[1] To whom all inquiries should be addressed.

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