Supplementary Material Available: A listing of atomic positional and thermal parameters at each temperature for the methanol and ethanol solvates, bond distances and angles in the ethanol solvate, and a listing at each temperature of observed and calculated structure factors for the methanol and ethanol solvates (74 pages). Ordering information is given on any current masthead page.

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Formation of Hydridocyclotriphosphazenes via the Reactions of Organocopper Reagents with Halocyclotriphosphazenes. Reaction Mechanism[1-3]

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Abstract: 1-Hydrido-1-alkyltetrachlorocyclotriphosphazenes, N$_3$P$_3$Cl$_4$RH (II) (where R = CH$_3$, C$_2$H$_5$, n-C$_3$H$_7$, i-C$_3$H$_7$, n-C$_4$H$_9$, i-C$_4$H$_9$, t-C$_4$H$_9$), have been synthesized by the new reaction of hexachlorocyclotriphosphazene, (NPCl$_2$)$_3$, with alkyl Grignard reagents in the presence of [(n-C$_4$H$_9$)$_3$PCuI]$_4$, followed by treatment with 2-propanol. The structural characterization of these compounds is discussed together with a detailed study of the reaction mechanism that permits hydridophosphazene formation. These reactions proceed via the formation of metallophosphazene intermediates. The nature of these complexes is discussed.

An important need exists for the development of new synthetic methods for the preparation of cyclic or open-chain phosphazenes that contain alkyl or aryl groups bonded directly to the skeleton through phosphorus–carbon bonds. Cyclic alkyl- or arylphosphazenes are of interest for fundamental reactivity studies, as models for thermally stable high polymers, or as "monomers" for polymerization studies.[4] The high polymers themselves are expected to constitute a new class of useful macromolecules.

A number of examples have been reported in the literature of reactions between halophosphazenes and Grignard or organolithium reagents.[5-18] Such reactions lead to alkylation or

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Table I. Hydridophosphazenes. NMR Data[a],[35]

compd	^{31}P NMR,[36] ppm[38]		^{1}H NMR,[41] δ[42]			coupling constants,[b] Hz
	P(R)H	PCl_2	hydride	alkyl		
$N_3P_3Cl_4(CH_3)H$[c,d]	13.8 (t)	17.6 (d)	7.44 (d, t, m)	$-CH_3$	1.75 (d, m)	J_{PH} = 568 J_{PCH} = 16 J_{PNP} = 12 J_{PNPH} = 11 J_{PNPCH} = 4 J_{HCPH} = 2.9
$N_3P_3Cl_4(C_2H_5)H$[c,d]	20.4 (t)	18.4 (d)	7.33 (d, t)	$-CH_2CH_3$ $-CH_2CH_3$	1.90 (m) 1.20 (d, t)	J_{PH} = 553 J_{PNPH} = 12 J_{PNP} = 8 J_{PCCH} = 23 J_{HCCH} = 7.5 J_{PCH} unresolved J_{PNPCH} unresolved
$N_3P_3Cl_4(n\text{-}C_3H_7)H$[d,e]	17.1 (t)	19.0 (d)	7.33 (d)	$-CH_2CH_2CH_3$ $-CH_2CH_2CH_3$	1.75 (m) 1.09 (t)	J_{PH} = 554 J_{PNPH} = 12 J_{PNP} = 8 other couplings unresolved
$N_3P_3Cl_4(i\text{-}C_3H_7)H$[c,d]	26.5 (t)	18.4 (d)	7.10 (d, t)	$-CH(CH_3)_2$ $-CH(CH_3)_2$	1.98 (m) 1.20 (d, d)	J_{PH} = 548 J_{PNPH} = 13 J_{PNP} = 8 J_{PCH} = 7.5 J_{PCCH} = 23 J_{HCCH} = 7.0
$N_3P_3Cl_4(n\text{-}C_4H_9)H$[d,e]	17.9 (t)	19.4 (d)	7.33 (d, t)	$-(CH_2)_3CH_3$ $-(CH_2)_3CH_3$	1.96 (m) 1.60 (t)	J_{PH} = 554 J_{PNPH} = 12 J_{PNP} = 4 J_{HCCH} = 18 other couplings unresolved
$N_3P_3Cl_4(i\text{-}C_4H_9)H$[d,e]	15.7 (t)	19.0 (d)	7.36 (d, t)	$CH_2CH(CH_3)_2$ $CH_2CH(CH_3)_2$	2.40 (m) 1.01 (d)	J_{PH} = 553 J_{PNPH} = 12 J_{PNP} = 6 J_{HCCH} = 20 other couplings unresolved
$N_3P_3Cl_4(t\text{-}C_4H_9)H$[c,d]	32.3 (t)	18.4 (d)	6.83 (d, t)	$-C(CH_3)_3$	1.17 (d)	J_{PH} = 543 J_{PNPH} = 13 J_{PNP} unresolved J_{PCCH} = 20

[a] d = doublet, t = triplet, m = multiplet. [b] Confirmed by homo- and heteronuclear decoupling experiments. [c] ^{31}P NMR spectrum run in THF solution. [d] ^{1}H NMR spectrum run in $CDCl_3$ solution. [e] ^{31}P NMR spectrum run in $CDCl_3$ solution.

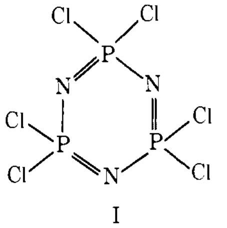
arylation, or to cleavage of the phosphazene skeleton. In many cases the substitution and cleavage reactions occur concurrently.[19] Our objective in this work was to find an alkylation or arylation system that would permit halogen atoms attached to a phosphazene ring or chain to be replaced in a controlled manner, without cleavage of the skeleton.

Organocopper reagents were chosen for this purpose because such species permit the selective replacement of halogen atoms in organic compounds by various alkyl or aryl residues.[20,21] The wide scope and effectiveness of these reagents have been discussed elsewhere.[20-29] Of all the methods available for the utilization of organocopper reagents, the "copper-catalyzed" Grignard reaction is the easiest to use. Hence, this system was chosen for our study.

Although the synthesis of alkylphosphazenes was the objective of this work it was discovered that reactions of this type provided a new and unusual route for the synthesis of *hydrido*phosphazene species,[3] compounds that have been synthesized before by only one reaction pathway.[30-33] Moreover, the synthesis described here is the only available method for the preparation of phosphazenes that contain both hydrido *and* halogeno groups. The use of hydridophosphazenes as synthetic intermediates is a subject of some consequence.

Results and Discussion

Overall Reaction. When hexachlorocyclotriphosphazene, $(NPCl_2)_3$, was allowed to react with alkyl Grignard reagents in the presence of $[n\text{-}Bu_3PCuI]_4$,[34] followed by treatment with 2-propanol, cyclophosphazenes were formed that possessed an



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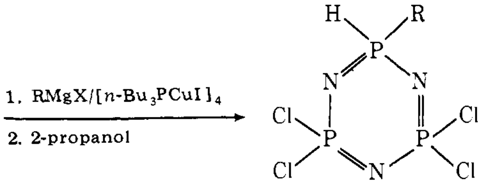


II

Table II. Hydridophosphazenes, Chracterization Data

compd	% yield	mp, °C	infrared data[a],44 ν_{PH}	ν_{PN}	mass spectral data45 found[b]	calcd[c]	elemental anal. found	calcd
$N_3P_3Cl_4(CH_3)H$	76	95	2409 (m) 2399 (m)	1220 (s) 1180 (s) 1160 (s)	291	291	C 3.98 H 1.40 N 14.23 P 31.65 Cl 47.45	C 4.13 H 1.37 N 14.33 P 31.74 Cl 48.46
$N_3P_3Cl_4(C_2H_5)H$	60	59	2399 (m) 2395 (m)	1228 (s) 1185 (s) 1170 (sh)	305	305	C 7.82 H 2.00 N 13.71 P 30.39 Cl 46.17	C 7.82 H 1.95 N 13.68 P 30.29 Cl 46.25
$N_3P_3Cl_4(n\text{-}C_3H_7)H$	68	62	2418 (m) 2399 (m)	1215 (s) 1178 (s) 1160 (s)	319	319	C 11.43 H 2.57 N 12.99 P 28.68 Cl 44.32	C 11.21 H 2.49 N 13.08 P 28.93 Cl 44.24
$N_3P_3Cl_4(i\text{-}C_3H_7)H$	69	65	2395 (m) 2380 (m)	1210 (s) 1185 (s) 1170 (s)	319	319	C 11.34 H 2.50 N 13.08 P 28.75 Cl 44.10	C 11.21 H 2.49 N 13.08 P 28.93 Cl 44.24
$N_3P_3Cl_4(n\text{-}C_4H_9)H$	58	43	2420 (m) 2405 (m)	1210 (s) 1185 (s) 1160 (sh)	333	333	C 14.22 H 3.00 N 12.57 P 27.87 Cl 41.94	C 14.33 H 2.98 N 12.54 P 27.76 Cl 42.39
$N_3P_3Cl_4(i\text{-}C_4H_9)H$[d]	36	oil	2401 (m) 2395 (m)	1225 (s) 1180 (s) 1165 (sh)	333	333		
$N_3P_3Cl_4(t\text{-}C_4H_9)H$[d]	55	39	2375 (m) 2365 (m)	1245 (s) 1200 (s) 1185 (s)	333	333		

[a] w = weak, m = medium, s = strong, br = broad, sh = shoulder. [b] As the base peak in a Cl_4 isotope pattern. [c] Calculated using $^{35}Cl_4$. [d] Elemental analysis could not be obtained on this compound owing to its low thermal stability.

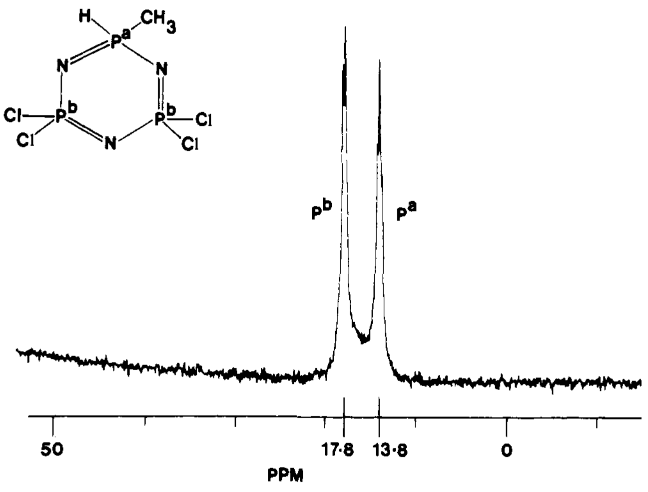


Figure 1. ^{31}P NMR spectrum of $N_3P_3Cl_4(CH_3)H$ (proton decoupled).

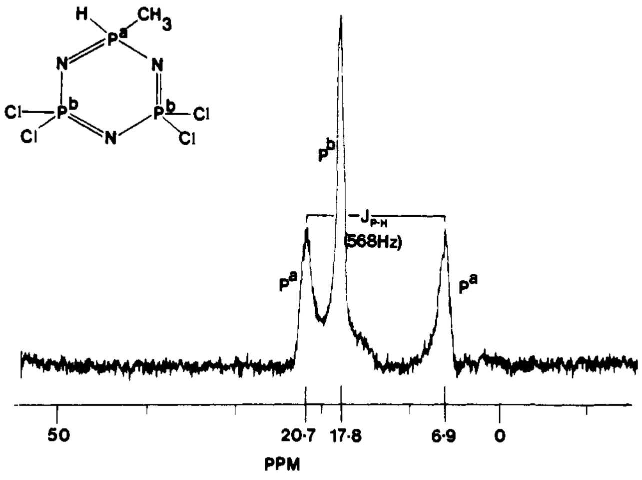


Figure 2. Proton-coupled ^{31}P NMR spectrum of $N_3P_3Cl_4(CH_3)H$.

alkyl group and a hydrido unit linked to one phosphorus atom (II). Compounds of structure II were prepared in which R is CH_3, C_2H_5, n-C_3H_7, i-C_3H_7, n-C_4H_9, i-C_4H_9, and t-C_4H_9. All these compounds are air- and moisture-sensitive, volatile products. When R is CH_3, C_2H_5, n-C_3H_7, i-C_3H_7, n-C_4H_9, or t-C_4H_9, they are white, crystalline compounds. The i-C_4H_9 product is a colorless oil.

Proof of Structure II. The structure of the hydridocyclotriphosphazenes (II) was determined unambiguously from ^{31}P and ^1H NMR spectra. The discussion of this structural proof will be limited to that of the methyl derivative, $N_3P_3Cl_4(CH_3)H$. The data for the other products are shown in Tables I and II.

Figure 1 shows the ^{31}P NMR spectrum of $N_3P_3Cl_4(CH_3)H$.[35,36] It is a simple AB_2 spin system,[37] with peaks at 17.6[38] (PCl_2 as a doublet with J_{PNP} = 12 Hz) and 13.8 ppm ($PHCH_3$ as a triplet with J_{PNP} = 12 Hz). The peak at 13.8 ppm was found to be significantly larger than expected, because of the nuclear Overhauser effect of the hydrogen atom bound to this phosphorus, and other relaxation effects.[39] In the proton undecoupled spectrum (Figure 2) the peak at 13.8 ppm was split into a doublet (J_{PH} = 568 Hz), with additional fine structure from the PNP and PCH couplings.

The phosphorus-decoupled ^1H NMR spectrum[41] of this compound (Figure 3) showed a CH_3 resonance at δ 1.75[42] (a doublet with J_{HPCH} = 2.9 Hz[43]) and the hydride resonance at δ 7.44 (a quartet with J_{HCPH} = 2.9 Hz). The phosphorus-undecoupled ^1H NMR spectrum (Figure 4) showed the CH_3

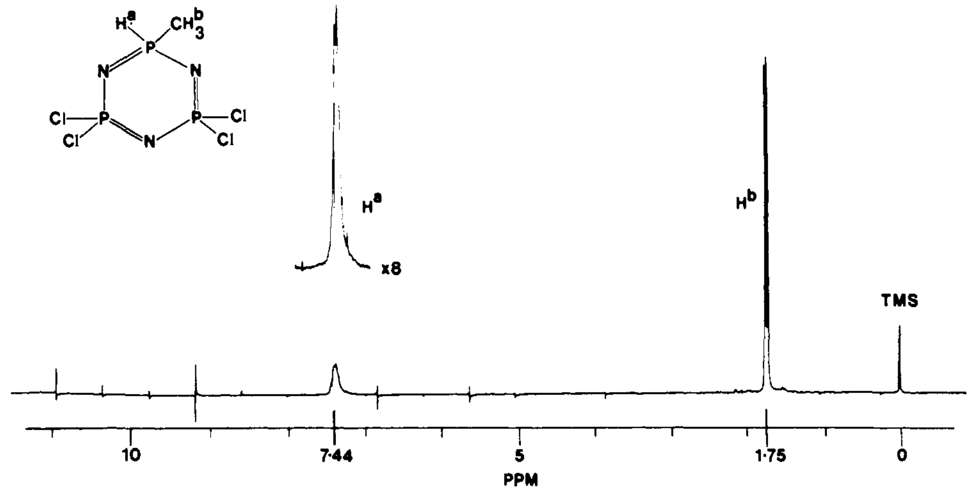


Figure 3. ^{1}H NMR spectrum of $N_3P_3Cl_4(CH_3)H$ (phosphorus decoupled).

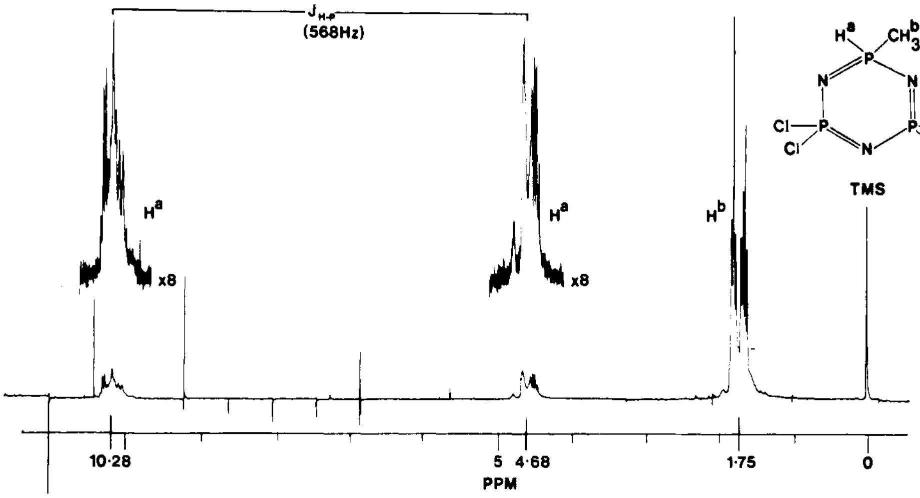


Figure 4. Phosphorus-coupled ^{1}H NMR spectrum of $N_3P_3Cl_4(CH_3)H$.

resonance split into a doublet of multiplets (J_{PCH} = 16, J_{PNPCH} = 4, J_{HPCH} = 2.9 Hz). In this spectrum the hydride resonance appeared as a doublet of triplets with additional fine structure (J_{PH} = 568, J_{PNPH} = 11, J_{HCPH} = 2.9 Hz). A further confirmation of these coupling constants was obtained from ^{1}H homodecoupled experiments.

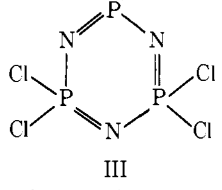
Although the NMR spectra provided unambiguous evidence for structure II, further confirmation of the structure was obtained from infrared spectra,[44] mass spectra,[45] and microanalytical data. This information is summarized in Table II and in the Experimental Section. Moreover, the structure of $N_3P_3Cl_4(i\text{-}C_3H_7)H$ was confirmed by a single-crystal X-ray structure determination. This will be discussed in a later paper.

Reaction Mechanism

The formation of hydridocyclotriphosphazenes (II) from these reactions was a surprising result that raised a number of questions. (1) What is the source of the hydrogen atom that yields the hydridophosphazene structure? (2) Is copper an essential prerequisite for this reaction and, if so, how does the copper participate in the synthesis? (3) What is the reaction pathway that leads to the formation of II?

Source of Hydrogen Atom Bound to Phosphorus. Initially, a number of experiments were carried out to determine the effect of Grignard concentration on the formation of II. The sequence of operations involved the addition of successive amounts of methylmagnesium chloride to a solution of $(NPCl_2)_3$ (I) and $[n\text{-}Bu_3PCuI]_4$, followed by vapor phase chromatographic analysis of the reaction mixture.[46] Surprisingly, it was found that, although the $(NPCl_2)_3$ was consumed in direct proportion to the amount of Grignard reagent added (up to 3-3.5 equiv per $(NPCl_2)_3$ molecule), no trace of II was detected, even after 24 h of reaction. However, when 2-propanol was added to the reaction mixture (ostensibly to destroy the excess Grignard reagent), compound II (R = CH_3) could be detected by vapor phase chromatography.[46]

This reaction sequence was then repeated with the use of $(CH_3)_2CHOD$. The product III was isolated. The incorporation of deuterium into III was demonstrated by the following results. A mass spectrum[45] showed a parent ion at m/e 292 as the base peak of the characteristic Cl_4 isotope pattern.[47] An infrared spectrum showed no band at 2400 cm^{-1} (P-H stretch) but showed instead a band at 1760 cm^{-1} that was assigned to the P-D stretch. The ratio ν_{PH}/ν_{PD} should be $\simeq\sqrt{2}$ on the



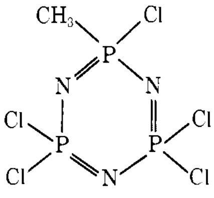
III

basis of a Hookes-law analysis. With compounds II (R = CH_3) and III the ratio is 1.363. The ^{31}P NMR spectrum[36] (in $CDCl_3$ solution with proton decoupling) showed a peak at 18.6 ppm (PCl_2 as a doublet with J_{PNP} = 12 Hz) and a peak at 11.4 ppm ($PDCH_3$ as a triplet, with J_{PD} = 85 Hz, of triplets with J_{PNP} = 12 Hz). The phosphorus-deuterium coupling constant was confirmed from the ^2H NMR spectrum[48] (in C_6F_6 solution with proton decoupling), which showed the deuterium resonance as a doublet, with J_{PD} = 85 Hz, centered at 1.71 ppm downfield from external C_6D_6. The observed difference between J_{PH} and J_{PD} is in good agreement with that found in other cases.[33,49] Finally, the ^1H NMR spectrum showed no P-H resonance, but gave the CH_3 resonance at δ 1.75 as a doublet of triplets (J_{PCH} = 16, J_{PNPCH} = 4 Hz), and this coupling pattern is in marked contrast to the multiplet structure observed for the methyl resonance of II (R = CH_3), as shown in Figure 4.

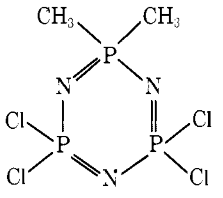
The incorporation of the deuterium atom into III showed unequivocally that the alcohol is the source of the hydrogen atom bound to the phosphorus in II. This led to the supposition that a nonvolatile metallophosphazene intermediate (i.e., nonvolatile in a vapor phase chromatography experiment) was present in solution before the addition of the alcohol. This prospect is considered in the following sections.

Involvement of Copper in the Reaction. The degree to which the formation of II was dependent on the concentration of $[n\text{-}Bu_3PCuI]_4$ was explored by means of the following experiments. A series of reactions was performed in which the molar ratio of methylmagnesium chloride to $(NPCl_2)_3$ was maintained at 4:1 but in which the amount of $[n\text{-}Bu_3PCuI]_4$ was increased. The results are shown in Figure 5. The maximum yields of II (R = CH_3) were obtained with copper atom to phosphazene ratios of more than 0.5:1.

When very low copper to phosphazene ratios (<0.15:1) were employed, it was found after the usual isolation procedure that the volatile products[50] consisted mainly of compounds IV and V rather than II (R = CH_3). Compounds IV and V are normally formed from the reaction of methylmagnesium chloride with $(NPCl_2)_3$ in the absence of copper. In such reactions the remainder of the product consists of ring-cleaved phosphazenes.[51] Thus, it appears that, at low copper concentrations, the trace of copper is removed by coordination to the phosphazene. The Grignard reagent then functions as if no copper were present, and reacts directly with the large amount of $(NPCl_2)_3$ in the system.



IV



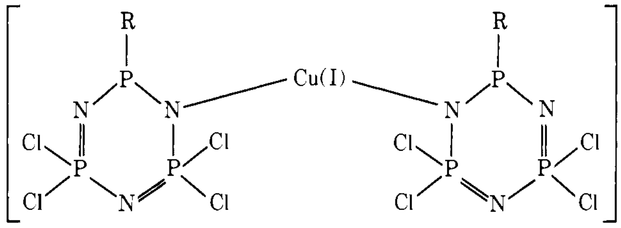
V

These results indicate that the copper does *not* play a *catalytic* role in the formation of II. On the contrary, it participates in the formation of a complex that functions as a reaction intermediate. In this respect, the copper behaves in a different manner from that normally assumed for many Grignard-copper system reactions.

Nature of the Metallophosphazene Intermediate. Two plausible possibilities exist for the mechanism of formation of a reactive copper-phosphazene intermediate. The intermediate could be generated by a direct interaction of $[n\text{-}Bu_3PCuI]_4$ with $(NPCl_2)_3$, or the mechanism could involve the essential participation of the Grignard reagent.

Two reactions were carried out in order to distinguish between these possibilities. In the first, $(NPCl_2)_3$ and $[n\text{-}Bu_3PCuI]_4$ were allowed to interact in stirred tetrahydrofuran. After 48 h, no reaction had taken place, as deduced by the absence of a change in the ^{31}P NMR spectrum of the reaction mixture. In the second reaction, increasing amounts of methylmagnesium chloride were added to a reaction mixture that contained $[n\text{-}Bu_3PCuI]_4$ and $(NPCl_2)_3$ in a copper atom to phosphazene ratio of 1:2. At the same time, the ^{31}P NMR spectrum was monitored. The changes are shown in Figure 6a. 2-Propanol was then added to each mixture (in the NMR tube) and the ^{31}P NMR spectrum was again obtained. These results are shown in Figure 6b. The spectra show clearly that the metallophosphazene complex is not formed until the Grignard reagent is added. Complexation is complete after the addition of a 3:1 excess of Grignard to phosphazene. The spectra also illustrate how treatment of this intermediate with 2-propanol leads immediately to the formation of II (R = CH_3).

The metallophosphazene intermediate was not isolated from the reaction mixture. However, we believe that its structure is similar to the one shown in VI. The evidence for this structure is as follows.

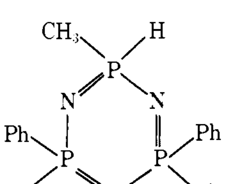


VI

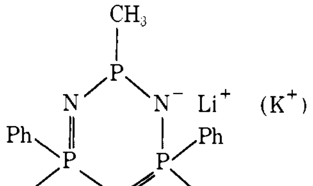
First, the stoichiometry of two phosphazene rings per copper atom was established from the data shown in Figure 5. The same conclusion is derived from the ^{31}P NMR results just described, in which a 2:1 ratio of phosphazene to copper was employed.

Second, the "cuprate" nature of the intermediate is compatible with its solubility in organic solvents such as THF and diethyl ether (many simple R-Cu type species are known to be insoluble in these media[20,21]) and from the fact that the metal must occupy a +1 oxidation state (copper(II) is reduced to copper(I) in the presence of organometallic reagents[20]).

Third, it seems reasonable to assume that the copper is bound to the phosphazene rings through the skeletal nitrogen atoms since these almost certainly represent the most electronegative sites in the molecule. This fact has been demonstrated elegantly by Schmidpeter and co-workers[32] by their isolation of compound VIII from the reaction of VII with $n\text{-}C_4H_9Li$ (or potassium). These same authors showed that VIII could be coupled to another phosphazene ring by means of a reaction with a P-Cl bond.[32] By contrast, species VI does not couple to a chlorophosphazene molecule, and this is compatible with a significant degree of covalent character in the phosphazene-copper bond.



VII



VIII

Fourth, additional evidence that VI contains copper-nitrogen bonds was obtained from the ^{31}P NMR spectrum (VI in Figure 6a). This spectrum shows three distinct phosphorus resonances, all broadened apparently due to coupling with the copper. This pattern is compatible with coordination to nitrogen rather than to tricoordinate phosphorus, where a simple AB_2 spin system would be expected.

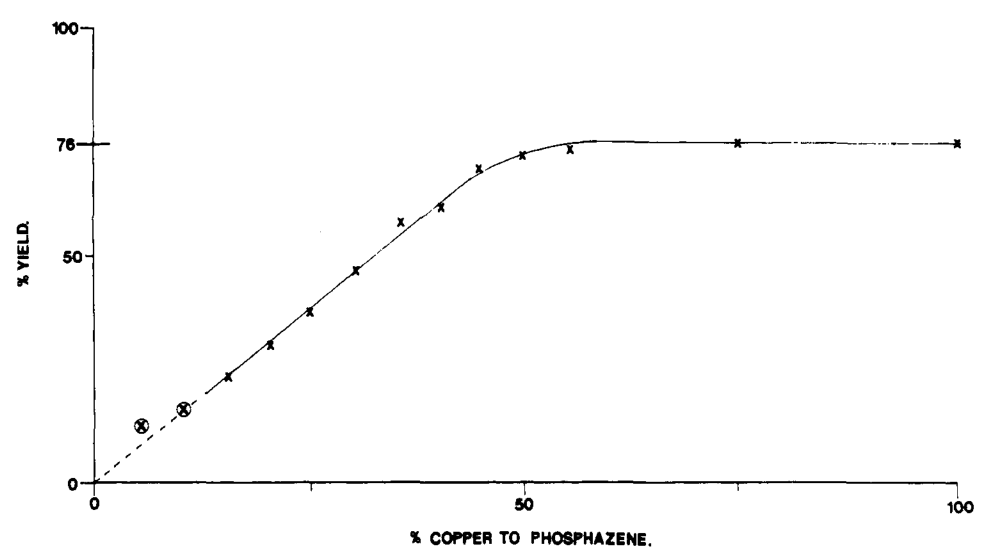


Figure 5. Curve showing the relationship between the percentage yield of $N_3P_3Cl_4(CH_3)H$ and the percentage of copper atoms to $(NPCl_2)_3$ molecules in the reaction mixture. For the circled points, see ref 55.

Figure 6. Changes in the ^{31}P NMR spectrum following the addition of increasing amounts of CH_3MgCl to a 1:8 ratio mixture of $[n\text{-}Bu_3PCuI]_4$ and $(NPCl_2)_3$. (a) Spectra of the reaction mixture before the addition of 2-propanol. (b) Spectra after the addition of 2-propanol.

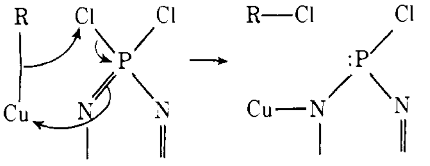
Of course, the possibility of additional coordination of copper to the phosphazene ring through the other skeletal nitrogen atoms or through the tricoordinate phosphorus atom cannot be ruled out. Moreover, the possibility also exists that the other coordination sites at copper could be filled by $n\text{-}Bu_3P$ molecules or by tetrahydrofuran, the reaction solvent.

Reactions with Methylcopper. In view of the mechanistic implications discussed in the preceding sections, it was of interest to determine if alkylcopper reagents would react with $(NPCl_2)_3$ in a manner different from that found for $[n\text{-}Bu_3PCuI]_4$.

Methylcopper was obtained by the reaction of methylmagnesium chloride with $[n\text{-}Bu_3CuI]_4$ at −80 °C.[21] A reaction with $(NPCl_2)_3$ in tetrahydrofuran at −80 to 25 °C, followed by treatment with 2-propanol, yielded the cyclophosphazenes,[50] $N_3P_3Cl_6$ (I), $N_3P_3Cl_5H$, and $N_3P_3Cl_4CH_3H$ (II). The isolation of $N_3P_3Cl_5H$ from this reaction system was a valuable clue to the reaction mechanism, as discussed in the following section.

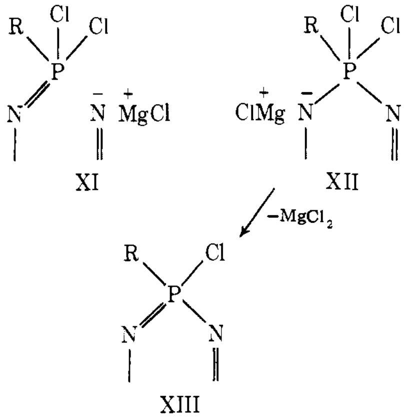
Reaction Pathway. The *exact* reaction pathway that leads to the formation of the metallophosphazene and, eventually, to the hydridophosphazene remains partly unsolved. For example, it is not known whether radical or ionic mechanisms are involved in the initial steps. However, sufficient evidence has been obtained to allow the overall mechanism to be understood.

It is presumed that, although $[n\text{-}Bu_3PCuI]_4$ is unreactive with $(NPCl_2)_3$, the reaction of $[n\text{-}Bu_3PCuI]_4$ with the Grignard reagent yields an alkylcopper compound, R-Cu. The yellow precipitate observed in these reactions is believed to be the alkylcopper compound. A reaction is then assumed to occur between the alkylcopper reagent and $(NPCl_2)_3$, as shown in IX and X. Significant quantities of the alkyl halides, R-Cl, were detected from the reaction mixture by the use of VPC/mass spectrometric analysis.[50] The coupled species, R-R, was also detected,[50] probably as a product from the reaction of R-Cl with the Grignard reagent or the organocopper compound.[20] In these terms, the formation of $N_3P_3Cl_5H$ by the interaction of $(NPCl_2)_3$ with methylcopper followed by protonation with 2-propanol provides evidence that a species of type X has a discrete existence after alkyl halide elimination occurs.



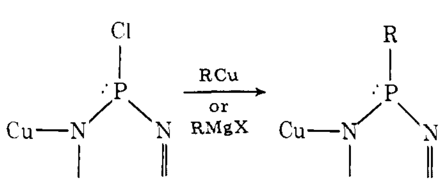
IX X

This metal-halogen exchange process is the key to the unique behavior of the organocopper reagent with chlorophosphazenes. Grignard reagents react with chlorophosphazenes to cause skeletal cleavage (XI), as well as alkyl-halogen exchange (XIII), because the alkyl group attacks at phosphorus (XII)[19,51,52] rather than at chlorine. By contrast, the alkylcopper species attacks the chlorine atom. At the same time, the copper atom is better able to stabilize the negative charge on nitrogen than is magnesium.



XI XII XIII

The initial metal-halogen exchange reaction is believed to generate X, a species with a trivalent, tricoordinate phosphorus atom. The chlorine remaining on this phosphorus can then be replaced readily by an alkyl group (in the form of R^-) from either the Grignard or the organocopper reagent, to yield XIV.



X XIV

The stoichiometry of the reaction requires that two phosphazene rings are associated with each copper atom. This could be accomplished by further alkylation of the copper in XIV to form a mixed "cuprate", which then undergoes a metal-halogen exchange reaction with a second phosphazene ring, and subsequent alkylation of the remaining "tricoordinate" P-Cl unit to yield VI. Thus, of the 3 equiv of Grignard reagent per phosphazene ring required for the complete reaction, 1 equiv is used for metalation, 1 equiv for the alkylation, and up to 1 equiv for the reaction with the alkyl halide to yield R-R.

The final step in the reaction pathway is the interaction of the metallophosphazene complex VI with a 2-propanol to yield II. The copper—phosphazene bond may be cleaved to generate an N-H unit which then rearranges rapidly to form the P-H tautomer, II. Attempts to detect the presence of the N-H form, by the use of NMR spectroscopy, were unsuccessful, and it appears that cleavage of the copper-nitrogen bond could be a slower step than rearrangement of the proton from nitrogen to phosphorus. The ability of a cyclophosphazene system to undergo N-H to P-H tautomerism is well documented.[30-32,54]

Aryl Grignard reagents did not participate in the same type of reaction, and no arylhydridocyclophosphazenes have yet been prepared by the organocopper route. Phenylmagnesium chloride reacted with $(NPCl_2)_3$ in the presence of $[n\text{-}Bu_3PCuI]_4$ to yield *gem*-$N_3P_3Cl_4Ph_2$ and ring-cleavage products.[19,53] Thus, in these reactions, phenylcopper appears to react in a way that is reminiscent of alkyl Grignard reagents.[53] The differences in reactivity between alkyl- and arylcopper reagents have been noted previously.[20]

Compounds of structure II or VI are valuable not only for their mechanistic and structural features, but also because of their use as general synthetic intermediates. These aspects will be discussed in a later paper.

Experimental Section

Materials. Hexachlorocyclotriphosphazene (I) was supplied by Ethyl Corp. and was purified by sublimation, followed by two recrystallizations from *n*-hexane. The Grignard reagents were commercial products obtained from Aldrich or Alfa-Ventron. Tetrahydrofuran was distilled into the reaction flask under an atmosphere of dry nitrogen from a sodium-benzophenone ketal drying agent. The reagent, $[n\text{-}Bu_3PCuI]_4$, was prepared by standard methods[34] and was recrystallized from 2-propanol/ethanol before use. All reactions were carried out under an atmosphere of dry nitrogen.

General Synthetic Route to Hydridophosphazenes. The syntheses of all the hydridophosphazenes were carried out in an identical manner. The following procedure is typical. Hexachlorocyclotriphosphazene (I, 5.0 g, 0.014 mol) and $[n\text{-}Bu_3PCuI]_4$ (3.0 g, 0.019 mol) were stirred together in tetrahydrofuran (150 mL) at −80 °C, and the Grignard reagent (10 mL of a 3 M solution in THF or ether) was added dropwise over a period of ≃30 min. The temperature was allowed to rise to ≃−30 °C, and a further 10 mL of the Grignard reagent was added. The reaction mixture was then stirred for 16 h and the temperature was allowed to rise to 25 °C. The mixture was then cooled to 0 °C and 2-propanol (10 mL) was added. Finally, removal of the solvent in vacuo and sublimation (or distillation) of the residues gave the hydridophosphazenes (II) in up to 76% yield. NMR data for all the compounds are summarized in Table I. Yields and analytical, mass spectral, and infrared data are summarized in Table II.

Initial Monitoring of the Reaction. Hexachlorocyclotriphosphazene (5.0 g, 0.014 mol) and $[n\text{-}Bu_3PCuI]_4$ (3.0 g, 0.0019 mol) were stirred together in tetrahydrofuran (150 mL) at 0 °C. An aliquot (5 μL) was withdrawn and was subjected to vapor phase chromatographic analysis. Methylmagnesium chloride (2 mL, 3.0 M solution of THF) was added and the reaction mixture was stirred for 30 min. Stirring was discontinued and any solid matter was allowed to settle to the bottom of the flask. An aliquot was again withdrawn (5 μL) and was subjected to vapor phase chromatographic analysis. The above sequence was repeated until 20 mL of the Grignard reagent had been added to the reaction mixture. At this time the reaction mixture was stirred for a further 48 h, with samples being withdrawn every 12 h for analysis. Finally, $(CH_3)_2CHOH$ (10 mL) was added and, after stirring for 30 min, the final aliquot (5 μL) was removed for vapor phase chromatographic analysis.

Identification of the Source of Hydrogen. A reaction was carried out as described in the general synthesis section. However, $(CH_3)_2CHOD$ (10 mL) was used in the final step. The isolation and purification steps were the same as described previously. The compound, $N_3P_3Cl_4(CH_3)D$ (III), was obtained as white, air- and moisture-sensitive needles, mp 93-94 °C, in 70% yield.

Variation in Copper Concentration. A series of reactions was carried out in which the amounts of phosphazene and added Grignard reagent were maintained constant, but the quantity of copper in the reaction mixture was varied. The amount of $(NPCl_2)_3$ used in each case was 5.0 g, with 20 mL of a 3 M solution of methylmagnesium chloride in THF. The reactions were carried out as described previously. The quantity of $[n\text{-}Bu_3PCuI]_4$ used in each reaction is summarized in Table III. The results are shown graphically in Figure 5.[55]

Attempted Reaction between $(NPCl_2)_3$ and $[n\text{-}Bu_3PCuI]_4$. Hexachlorocyclotriphosphazene (5.0 g, 0.014 mol) was dissolved in THF (100 mL) at room temperature. A sample of this solution was removed and its ^{31}P NMR spectrum was obtained.[36] The spectrum consisted of a singlet at 19.8 ppm which was characteristic of unchanged $(NPCl_2)_3$.[38] A sample of $[n\text{-}Bu_3PCuI]_4$ (3.0 g, 0.019 mol) was also dissolved in THF (100 mL) and its ^{31}P NMR spectrum (broad band proton decoupled) was scanned.[36] The spectrum showed a broad singlet centered at −34 ppm.[38] These two solutions were mixed and the ^{31}P NMR spectrum of the resultant solution showed only peaks from $(NPCl_2)_3$ and $[n\text{-}Bu_3PCuI]_4$. No peak shift or other change occurred in the spectrum after 48 h of stirring. Thus, it was concluded that no reaction had occurred.

^{31}P NMR Monitoring of the Complete Reaction. To the mixture obtained from the above experiment was added methylmagnesium chloride in 2.5-mL aliquots (3.0 M solution in THF). After each ad-

Table III. Influence of Copper Concentration on Yield of $N_3P_3Cl_4CH_3H$

[n-$Bu_3PCuI]_4$ in reaction mixture		product yield	
wt, g	% Cu/phosphazene	wt, g	%[a]
0.28	5	0.50	12[b]
0.56	10	0.63	15[b]
0.84	15	0.95	23
1.12	20	1.25	30
1.40	25	1.60	38
1.68	30	1.93	46
1.96	35	2.40	58
2.25	40	2.55	61
2.52	45	2.93	70
2.80	50	3.06	74
3.08	55	3.04	74
4.20	75	3.12	76
5.50	100	3.15	76

[a] Calculated for $N_3P_3Cl_4(CH_3)H$. [b] See ref 55.

dition a sample (3 mL) was removed and its ^{31}P NMR spectrum was scanned (Figure 6a). 2-Propanol (1.0 mL) was then added to the mixture in the NMR tube and the spectrum was scanned again (Figure 6b).

Reaction of $(NPCl_2)_3$ with Methylcopper. The reagent, [n-$Bu_3PCuI]_4$ (11 g, 0.0069 mol), was dissolved in THF (150 mL) and was cooled to −80 °C. Methylmagnesium chloride (10 mL, 3.0 M solution in THF) was then added dropwise. The rapid formation of methylcopper was evident from the deposition of a heavy yellow precipitate. After the mixture had been stirred for 30 min, $(NPCl_2)_3$ (5.0 g, 0.014 mol), dissolved in THF (100 mL), was added rapidly to the suspension of methylcopper at −80 °C. The reaction mixture was stirred for a further 16 h, during which time the temperature was allowed to rise to 25 °C. Finally, $(CH_3)_2CHOH$ (10 mL) was added to the mixture, which was then stirred for a further 30 min. Removal of the solvent under vacuum and sublimation of the residue gave a mixture of products. This was analyzed by gas chromatography/mass spectrometry and was found to consist of $(NPCl_2)_3$, $N_3P_3Cl_5H$, and $N_3P_3Cl_4(CH_3)H$.

Isolation of Gaseous Side Products. A reaction was carried out between $(NPCl_2)_3$, methylmagnesium chloride, and [n-$Bu_3PCuI]_4$ at 0 °C in THF with the molar ratios as described earlier (general synthetic route). However, the reaction was carried out under a nitrogen atmosphere, but in a closed reaction vessel connected via an oil "bubbler" to a water-filled gas collection vessel. After addition of the Grignard reagent, the reaction mixture was stirred for 30 min, after which time gas evolution had almost ceased. A total of approximately 150 mL of gas was collected. Samples of the gas were withdrawn from the collection vessel and were subjected to gas chromatography/mass spectrometric analysis. Chloromethane, ethane, and a trace of methane were detected. In two control experiments, (a) $(NPCl_2)_3$ and MeMgCl were allowed to react,[51] and (b) methylmagnesium chloride was added to a solution of [n-$Bu_3PCuI]_4$ at 0 °C. In neither case was chloromethane detected.

Use of Phenylmagnesium Chloride. Hexachlorocyclotriphosphazene (5.0 g, 0.014 mol) and [n-$Bu_3PCuI]_4$ (3.0 g, 0.0019 mol) were dissolved in THF (150 mL) and the mixture was cooled to −80 °C. Phenylmagnesium chloride (20 mL, 3.0 M solution in THF) was added slowly and the reaction mixture was stirred for 16 h, during which time the temperature was allowed to rise to 25 °C. Finally, $(CH_3)_2CHOH$ (10 mL) was added to the mixture. Removal of the solvent and sublimation of volatile products from residue gave $N_3P_3Cl_4Ph_2$ (identified by mass spectrometry) in very low yield.

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(43) This coupling constant was given as 3–4 Hz in an earlier communication.[3] However, a more accurate value for this coupling constant is now available owing to our recent acquisition of ^{31}P decoupling circuits on the ^1H NMR probe.
(44) Infrared spectra were recorded on a Perkin-Elmer 580 infrared spectrometer and were run as KBr disks.
(45) Mass spectra were recorded on an AEI MS-902 mass spectrometer operating at 70 eV ionizing potential.
(46) Vapor phase chromatographic data were obtained using a Hewlett-Packard Model 5750 chromatographic instrument fitted with a 6 ft 10% OV17 column and a thermal conductivity detector. The injection port was at 250 °C, the helium carrier gas flow rate was 2.5 mL min^{-1}, and the oven temperature range was 50–250 °C at 20 °C min^{-1}, following a 3-min postinjection interval.
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Nickel–Boron "Hybrid" Clusters. Synthesis of Polyhedral Nickelaboranes and Nickelacarboranes from Small Borane and Carborane Anions. Crystal Structure of $(\eta^5\text{-}C_5H_5)_4Ni_4B_4H_4$

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Abstract: Insertion of two to four nickel atoms into polyborane cages has been accomplished by reactions of metal reagents with the $B_5H_8^-$ and $(CH_3)_2C_2B_4H_5^-$ ions in tetrahydrofuran followed by air oxidation. Treatment of NaB_5H_8 with $NiBr_2$ and NaC_5H_5 generates *closo*-1,6-$(\eta^5\text{-}C_5H_5)_2Ni_2B_8H_8$ and *closo*-1,7-$(\eta^5\text{-}C_5H_5)_2Ni_2B_{10}H_{10}$, and the reaction of NaB_5H_8 with $(\eta^5\text{-}C_5H_5)_2Ni$ and sodium amalgam gives *closo*-$(\eta^5\text{-}C_5H_5)_4Ni_4B_4H_4$ and *nido*-$(\eta^5\text{-}C_5H_5)_4Ni_4B_5H_5$. Nickelocene and $Na(CH_3)_2C_2B_4H_5$ yield *closo*-$(\eta^5\text{-}C_5H_5)_2Ni_2(CH_3)_2C_2B_4H_4$ and *nido*-$(\eta^5\text{-}C_5H_5)_2Ni_2(CH_3)_2C_2B_5H_5$. The new compounds were structurally characterized from their ^{11}B and ^1H pulse Fourier transform NMR, IR, and low- and high-resolution mass spectra and an X-ray crystal structure determination on $(\eta^5\text{-}C_5H_5)_4Ni_4B_4H_4$. The latter molecule has closo-D_{2d} cage geometry despite the presence of 20 skeletal valence electrons, from which a nido structure would be predicted on the basis of electron counting rules. Its analogue $(\eta^5\text{-}C_5H_5)_2Ni_2(CH_3)_2C_2B_4H_4$ also has been assigned a D_{2d} closo structure, but $(\eta^5\text{-}C_5H_5)_4Ni_4B_5H_5$ is a nido (monocapped square antiprism) cage system, and its counterpart $(\eta^5\text{-}C_5H_5)_2Ni_2(CH_3)_2C_2B_5H_5$ probably has a similar cage geometry. The Ni_4B_4 and Ni_4B_5 clusters are the second and third examples (after $(\eta^5\text{-}C_5H_5)_4Co_4B_4H_4$) of tetrametallic metalloboron cages, and are hybrid systems related to both the metal clusters and the boranes. In $(\eta^5\text{-}C_5H_5)_4Ni_4B_4H_4$ the nickel atoms occupy low-coordinate vertices in the D_{2d} polyhedron, in contrast to $(\eta^5\text{-}C_5H_5)_4Co_4B_4H_4$, where the cobalt atoms occupy the high-coordinate positions. The Ni–Ni distance of 2.354 (1) Å is the shortest known metal–metal link in any type of metalloboron polyhedron, and may indicate localized metal–metal bonding. Crystal data for $(\eta^5\text{-}C_5H_5)_4Ni_4B_4H_4$ follow: space group $C2/c$, $Z = 4$, $a = 19.546\ (4)$ Å, $b = 7.512\ (4)$ Å, $c = 14.86\ (1)$ Å, $\beta = 106.70\ (2)°$, $V = 2090\ (2)$ Å^3, $R = 0.043$ for the 1500 reflections for which $F_o^2 \geq 3\sigma(F_o^2)$.

Metal-rich metalloboron polyhedra are compositionally intermediate between the polyhedral boranes and the metal clusters, and may be regarded as "hybrid" species which in a structural and electronic sense are members of both families.[1] The stable existence of such compounds provides concrete support for the thesis, first advanced by Wade[2] and subsequently developed by several authors,[3] that the metal cluster, organometallic cluster, and borane families are related electronically and are amenable to the same kind of molecular orbital description. This idea is the basis for the widely used electron-counting rules[3a] that correlate cage structure with framework electron population.

A continuing research interest in our laboratory has been the synthesis and structural characterization of transition metal–boron hybrid clusters, and a number of such species have been obtained from the treatment of $B_5H_8^-$ ion with metal ions in the presence of $C_5H_5^-$ in tetrahydrofuran (THF). With $CoCl_2$[4,5] the main isolable product was the monocobalt complex 2-$(\eta^5\text{-}C_5H_5)CoB_4H_8$, which was further metalated to give the first known closo metalloboranes including $(\eta^5\text{-}C_5H_5)_2Co_2B_4H_6$, $(\eta^5\text{-}C_5H_5)_3Co_3B_3H_5$, $(\eta^5\text{-}C_5H_5)_3Co_3B_4H_4$, and $(\eta^5\text{-}C_5H_5)_4Co_4B_4H_4$; our earlier structural assignments[4,5] for these molecules have been confirmed crystallographically.[6] With $FeCl_2$,[7] only monometallic products have been isolated from the $B_5H_8^-$ reaction, notably 2-$(\eta^5\text{-}C_5H_5)FeB_5H_{10}$ (a ferrocene analogue) and $(\eta^5\text{-}C_5H_5)FeB_{10}H_{15}$. With $NiBr_2$ the products did not correspond to those obtained in either the iron or cobalt systems, and the nickelocene–$B_5H_8^-$ reaction in the presence of sodium amalgam gave still different results.

The cobalt and iron systems have been fully described elsewhere,[4,5,7] and a preliminary communication on the nickelocene–$B_5H_8^-$ reaction has appeared.[8] In this article we present a detailed account of several reactions involving nickel insertion into the $B_5H_8^-$ and $(CH_3)_2C_2B_4H_5^-$ ions, including the structural characterization of the nickelaborane and nickelacarborane products.

Results and Discussion

Preparation of *closo*-1,7-$(\eta^5\text{-}C_5H_5)_2Ni_2B_{10}H_{10}$ and *closo*-1,6-$(\eta^5\text{-}C_5H_5)_2Ni_2B_8H_8$ from B_5H_8, $NiBr_2$, and $C_5H_5^-$. Our initial attempts to effect nickel insertion into the $B_5H_8^-$ ion utilized nickel bromide and sodium cyclopentadienide in THF solution at room temperature, from which two dinickel closo boranes were isolated in low yield by column chromatography along with traces of other products.

$$\begin{aligned}&B_5H_8^- + Ni^{2+} + C_5H_5^- \rightarrow\\ &\qquad \underset{\text{yellow (I)}}{(\eta^5\text{-}C_5H_5)_2Ni_2B_{10}H_{10}} + \underset{\text{orange (II)}}{(\eta^5\text{-}C_5H_5)_2Ni_2B_8H_8}\\ &\qquad\qquad + \underset{\text{brown (trace, III)}}{(\eta^5\text{-}C_5H_5)_2Ni_2B_{10}H_{10}}\end{aligned}$$

The yellow product I is an isomer of a brown compound, $(\eta^5\text{-}C_5H_5)_2Ni_2B_{10}H_{10}$, recently obtained by Hawthorne et al. from the reaction of nickelocene and $B_{10}H_{10}^{2-}$ ion.[9] The ^{11}B and ^1H NMR spectra of I (Tables I and II) indicate mirror or twofold symmetry and are consistent with a closo 12-vertex (icosahedral) structure analogous to $C_2B_{10}H_{12}$, but do not