Conclusion

In a previous publication,[25] it was pointed out that CIDNP polarization in homogeneous photolysis often predicts the appearance of products in significant yields with micellar irradiations in contrast to the insignificant yields in homogeneous photolyzate analysis. In this work, we observe that PPA and DPP stereoisomers are indeed formed in substantial amounts during the photolysis of DPP in micelle solutions (and in other super-cage environments) despite the fact that these products are present to less than 1% of total photoproducts in pentane irradiations. The styrene polarization in the CIDNP spectrum (Figure 1) produced by irradiation of DPP in C_6D_6 is consistent with the operation of two disproportionation mechanisms for formation of styrene. In pentane, the amount of PPA that accompanies styrene formation is twenty times less than the corresponding ethylbenzene formed, suggesting that most of the styrene arises from path c′ followed by path g. However, in SDS and porous silicates (Table VI), about 20–40% of the styrene produced is accompanied by PPA formation (the values are 70–80% for low-temperature photolysis), suggesting that path b to styrene is becoming significant due to the super-cage environment.

Finally, we note that these studies have demonstrated that the magnetic field effects for radical-pair recombinations are not restricted to only micellar solutions but are more like a general property of the restricted space provided by super-cage environments.[26] This confirms the notion that a magnetic field effect on micelle structures is not the dominant cause for effects previously noted in DBK ^{13}C-enrichment[6] and benzylic radical pair coupling studies.[23]

Acknowledgment. We thank the National Science Foundation for its generous support of this research. We also thank Drs. Gary Lehr and Eugene Sitzmann for helpful discussions.

Registry No. *meso*-DPP, 84454-38-6; *d,l*-DPP, 84454-39-7; TPB, 62640-72-6; α-MeDBK, 13363-25-2; $PhCH_2COCH_2Ph$, 102-04-5; $Ph\bar{C}HCO\bar{C}HPh{\cdot}Li^+{\cdot}K^+$, 64020-30-0; SDS, 151-21-3; HDTCl, 112-02-7.

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Cyclic and High Polymeric *nido*-Carboranylphosphazenes as Ligands for Transition Metals[1]

Harry R. Allcock,* Angelo G. Scopelianos, Robert R. Whittle, and Norris M. Tollefson

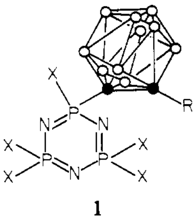
Contribution from the Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802. *Received May 6, 1982*

Abstract: 1-Methyl-1-(2-propynyl)-3,3,5,5-tetrachlorocyclotriphosphazene (**6**) reacts with bis(acetonitrile)–decaborane to yield 1-methyl-1-[(*o*-carboranyl)methylene]-3,3,5,5-tetrachlorocyclotriphosphazene (**7**). Species **7** was converted by base to the *nido*-carboranyl anion or dianion derivatives, which react with $Rh(PPh_3)_3Cl$ or with $Mo(CO)_6$ or $W(CO)_6$ to form the appropriate (metallocarboranyl)phosphazene derivatives (**10** or **12**). Compound **7** polymerizes when heated, and the high polymeric analogues (**13**, **14**, and **16**) behave in a similar manner to the cyclotriphosphazene derivatives in the formation of metallocarboranyl derivatives. Species **7** is unusual in its reaction with piperidine. The four halogen atoms are replaced by piperidino groups, and a boron atom is removed from the cage, but an internal counterion at skeletal nitrogen is generated rather than the expected piperidinium ion. An X-ray structural investigation of this species (**8**) confirmed the presence of a planar cyclotriphosphazene ring linked to the carboranyl unit through a methylene spacer group. A proton was connected to the phosphazene skeletal nitrogen atom furthest from the carboranyl group. The P–N bonds adjacent to the site of the carborane attachment were of normal length (1.575 Å), but the two bonds furthest from this site were exceptionally long (1.68 Å), presumably a consequence of ring protonation.

Complexes between *nido*-carboranyl structures and transition metals are well-known.[2-4] Recently we reported the first syntheses of *closo*-carboranes linked through C–P bonds to both cyclic and high polymeric phosphazenes.[5] In this present paper, we explore the prospect that *nido*-anion-species derived from carboranylphosphazenes might function as ligands for transition metals. Such compounds may be of interest as high-temperature, immobilized-catalyst species or as prototypes for polymers with unusual electrical behavior.

The objectives of this study were (1) to determine if neutral carboranylphosphazenes could be converted to the *nido*-anion species by strategies similar to those employed for the free carborane,[3] without decomposition of the phosphazene unit; (2) to identify the site of B–H bond loss from the neutral carboranyl unit; (3) to determine if a *nido*-carboranylphosphazene anion would function as a π ligand for transition metals; (4) to deduce if the phosphazene unit (with its σ-donor nitrogen atoms) might interfere with the metal coordination process; and (5) to explore the applicability of this chemistry to high polymeric analogues.

In the earlier work from our laboratory,[5] compounds of types **1** and **2** were prepared, where R = Me or Ph and X = Cl or OCH_2CF_3. These compounds formed the starting point for our



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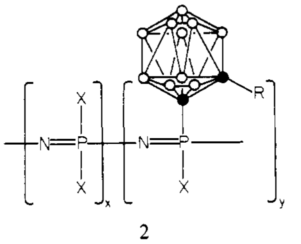

2

○ = BH; ● = C

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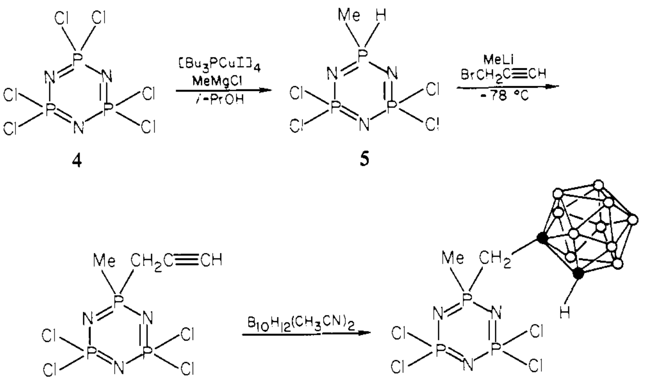
Scheme I



4

5

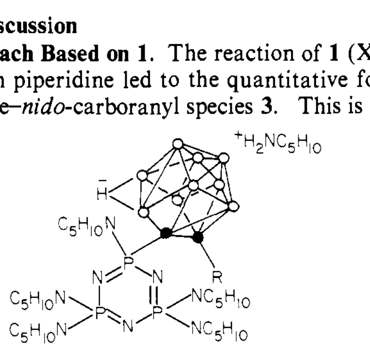
6

7, ○ = BH; ● = C

present studies, although, as will be shown, these species proved to be the least desirable starting materials for transition-metal binding. Thus, new synthetic strategies had to be developed.

Results and Discussion

Initial Approach Based on 1. The reaction of **1** (X = Cl, R = Me or Ph) with piperidine led to the quantitative formation of the phosphazene–*nido*-carboranyl species **3**. This is reminiscent of the behavior of free *o*-carborane.[6] Evidence for the formation of **3** was obtained from infrared, ^{31}P NMR, mass spectral, and microanalytical data. For example, the infrared spectrum of **3** showed peaks at 3310 cm^{-1} (w) (N—H), 2930 and 2850 cm^{-1} (s) (C—H), 2530 cm^{-1} (s) (B—H), and 1260 cm^{-1} (s) (P=N). The ^{31}P NMR spectra consisted of an AB_2 pattern with A centered at 22.0 ppm and B at 14.0 ppm. The mass spectral and microanalytical data are summarized in the Experimental Section. However, anion **3** failed to react with $Rh(PPh_3)_3Cl$ under a variety of reaction conditions (see Experimental Section). A study of molecular models suggested that the open face of the carboranyl anion unit was sterically shielded by the piperidino side groups attached to the phosphazene ring. Hence, alternative approaches were employed for the synthesis of analogues of **3** in which the carboranyl and phosphazene units were separated by a methylene "spacer" linkage.

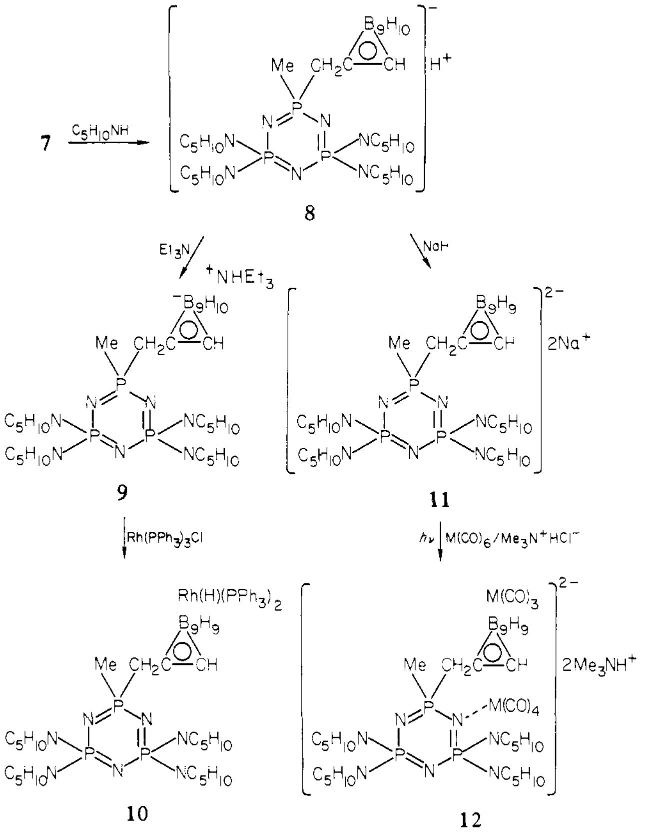


3, ○ = BH; ● = C

Introduction of the Methylene Linkage. In earlier work, we developed synthetic routes to hydridophosphazenes and various alkylphosphazenes on the basis of the reactions of organocopper–phosphazene complexes.[7,8] One species isolated in that work was **6**, formed as outlined in Scheme I. The interaction of **6** with bis(acetonitrile)–decaborane[9] gave **7** in high yield.

The structure of **7** was established from infrared, ^{31}P NMR, mass spectral, and microanalytical data. The infrared spectrum of **7** showed peaks at 3060 cm^{-1} (w) (C—H of the carborane), 2990–2900 cm^{-1} (w) (C—H), 2590 and 2550 cm^{-1} (s) (B—H), 1210 and 1180 cm^{-1} (s) (P=N), and 590 and 510 cm^{-1} (s) (P—Cl). The ^{31}P NMR spectrum consisted of an AB_2 pattern with A centered at 30.0 ppm and B at 19.0 ppm. The mass spectral and microanalytical data are summarized in the Experimental Section.

Scheme II



8

9

11

10

12

***nido*-Carborane Formation.** It was first necessary to concurrently open the carborane cage and remove the chlorine atoms in **7** to reduce the possibility of side reactions at these sites. These two steps were accomplished by treatment of **7** with piperidine to yield **8** (Scheme II).

Species **8** is anomalous in the absence of the piperidinium cation (in contrast to **3**). Instead, the proton counterion is associated with basic sites on the phosphazene skeletal unit. This unusual structure was identified by a combination of mass spectrometric, infrared, ^{31}P NMR, and microanalytical data (see Experimental section) and was confirmed by a single-crystal X-ray analysis. The mass spectrum revealed a parent ion that corresponded to species **8**. Like compound **3**, species **8** yielded an AB_2 ^{31}P NMR pattern with A centered at 39.4 ppm and B at 13.5 ppm.

Although compound **8** yielded a simple AB_2 ^{31}P NMR spectrum in tetrahydrofuran solvent, the coupling became increasingly complicated as the solvent was changed. For example, the spectrum of **8** in $CDCl_3$ collapsed to an ABB′ spin system, with A centered at 39.5 ppm, B at 14.5 ppm, and B′ at 13.6 ppm. The proton-coupled ^{31}P NMR spectrum of the same sample showed broader peaks, as expected. However, selective decoupling of the proton linked to the phosphazenyl nitrogen atom restored the coupling of only the BB′ portion of the spectrum. This suggested that this proton occupies a fixed position in $CDCl_3$ solvent. The asymmetry observed in these spectra was attributed to a solvation effect involving this protonated site.

Treatment of **8** with triethylamine gave the conventional triethylammonium salt **9**, and reaction with sodium hydride generated the disodium salt of the dianion (**11**).[4] Evidence for the formation of **9** was obtained from infrared, ^{31}P NMR, and microanalytical data. The ^{31}P NMR spectrum consisted of an AB_2 spin system, with A centered at 34.0 ppm and B at 17.0 ppm. Similarly, treatment of **8** with sodium hydride in tetrahydrofuran led to the evolution of hydrogen and formation of species **11**, with an AB_2 ^{31}P NMR spectrum. Peak A was centered at 32.2 ppm and B was at 19.0 ppm.

General Features of the Molecular Structure of 8. All structural features of the molecule were identified during the X-ray structure solution. The phosphazene ring in this structure is planar. The

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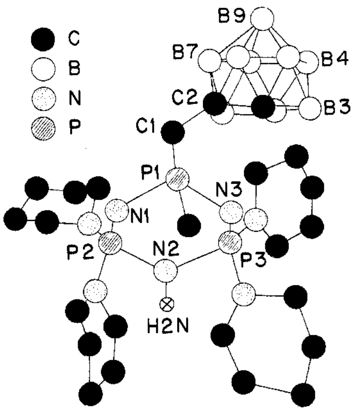

Figure 1. General structure and atom designations for **8**.

methyl group and methylene–unideca-*o*-carborane unit are linked to the same phosphorus atom through P–C bonds. Two piperidino groups are bound to each of the remaining phosphorus atoms through N–P bonds. The cyclotriphosphazenyl skeletal nitrogen atom furthest from the site of attachment of the alkyl groups bears a hydrogen atom that was identified and located unambiguously. This protonation causes an elongation of the adjacent P–N skeletal bonds. No significant distortion of the carboranyl cage was evident. However, it is of interest that although the open face of the carborane lies near the geminal methyl group, sufficient space exists, even in this conformation, to allow a transition metal to coordinate to the carborane. Thus, the methylene spacer does serve to open up the structure in a way that permits the binding of transition metals. As discussed later, this was confirmed by the synthesis of such adducts. The overall structure and principal atom designations are shown in Figure 1. A stereoscopic view appears in the supplementary material Figure 2. Table I (supplementary material) contains a listing of observed and calculated structure factors. Table II (supplementary material) is a tabulation of the positional and thermal parameters. Tables III and IV (supplementary material) contain listings of the most important bond lengths and angles.

Bonding Features in 8. The P–C bonds that link the methyl and methylene units to the phosphazene ring are of normal length (1.79 and 1.81 Å, respectively) and are consistent with values reported for other alkylcyclotriphosphazenes.[10,11] Thus, no unusual through-bond electronic interaction occurs between the carborane unit and the phosphazene ring. Similarly, the exocyclic P–N bonds that bind the piperidino units to the phosphazene ring are comparable in length (1.62 Å) to those reported for other related aminocyclophosphazenes.[12] The bond lengths within the phosphazene ring fall into two classes. The four that are closest to the alkylated phosphorus atom are unremarkable (1.54–1.60 Å) and correspond well to values reported for other alkyl- and aminocyclotriphosphazenes. However, the two distal P–N bonds are extremely long (1.68 Å) and are more reminiscent of those expected for exocyclic P–N bonds. Undoubtedly, this is a consequence of protonation at N2, which reduces the d_π–p_π character of the P2–N2–P3 segment and generates a phosphaz*ane* moiety. The existence of this proton was confirmed by residual electron density detected at this site during the final difference Fourier analysis. The N2–H bond distance is 0.7 Å. Thus, although this mode of protonation is unexpected, the X-ray results confirm the conclusions derived from the ^{31}P NMR, mass spectral, and microanalytical data. Within the carborane cage, the **B**–B bond lengths (average 1.77 Å) and internal acute angles (60°) are normal, which indicates no unusual interactions between this unit and the rest of the molecule.

Metal Coordination. Species **9** reacted cleanly with the tris(triphenylphosphine)rhodium(I) chloride in boiling ethanol to give **10** in high yield. This is reminiscent of the behavior of free *nido-o*-carborane.[13,14] A confirmation of the structure of **10** was obtained from infrared, ^{31}P NMR, ^1H NMr, and microanalytical data. For example, the infrared spectrum of **10** contained absorptions characteristic of triphenylphosphine, carborane, and piperidine-substituted phosphazene units, with an additional weak band at 2050 cm^{-1} assigned to RhH. The ^1H NMR spectrum of **10** in CD_2Cl_2 consisted of a complex series of resonances at 7.3 ppm assigned to the phenyl protons and broad resonances at 2.9 and 1.4 ppm from carboranyl and piperidino protons, respectively. The hydride resonance was observed at −8.6 ppm as a triplet of doublets with J_{Rh-H} = 16 Hz.[13] The ^{31}P NMR spectrum of **10** displayed an AB_2 pattern, assigned to the phosphorus atoms in the ring, with A at 29.0 ppm and B at 16.0 ppm. At 34.5 ppm a doublet of doublets was observed, attributed to coupling between the rhodium atom and triphenylphosphine units (J_{Rh-P} = 112 Hz) with phosphorus–hydrogen coupling (J_{P-H} = 24 Hz).

Treatment of **11** in tetrahydrofuran with $W(CO)_6$ or $Mo(CO)_6$ at 25 °C during ultraviolet irradiation resulted in the formation of a yellow color and evolution of carbon monoxide.[4] Subsequent treatment of these solutions with aqueous trimethylammonium chloride yielded brown (Mo) or red (W) salts of structure **12**. An indication of the structure of **12** was obtained from infrared, ^{31}P NMR, and elemental microanalysis. For example, the infrared spectrum of **12** contained absorptions at 3290 cm^{-1} (m) (N—H), 2940 and 2840 cm^{-1} (s) (C—H), 2500 cm^{-1} (s) (B—H), 2050 (w), 2035 (m), 1970 (s), 1920 (s), 1870 (s) (C≡O), and 1250 cm^{-1} (s) (P═N). The ^{31}P NMR spectra consisted of an ABX pattern with A centered at 41.5 ppm, B at 14 ppm, and X at 11.0 ppm. The microanalytical data are summarized in the Experimental Section.

The trimethylammonium salts of these anions were unstable in air but could be manipulated under a nitrogen atmosphere. The evidence suggests that in **12**, coordination of the dicarbollide ion to the metal occurs as expected,[4] with additional coordination of a metal tetracarbonyl unit to phosphazenyl skeletal nitrogen atoms. The quantitative consumption of two metal hexacarbonyl units per cyclophosphazene molecule, coupled with the appearance of at least six distinct C≡O absorptions in the infrared spectrum, provided evidence for this structure. Moreover, the appearance of an ABX pattern in the ^{31}P NMR spectra suggests the presence of three nonequivalent phosphorus atoms. This observation is compatible with previous work[15] in which molybdenum hexacarbonyl reacted with alkylated cyclophosphazenes to yield species in which molybdenum tetracarbonyl units were coupled to the phosphazene nitrogen atoms.

High Polymeric Analogues. In earlier work,[5] it was shown that species of type **1** (X = Cl) polymerize when heated to yield open-chain macromolecules bearing the carborane units as pendent groups. Compound **7** undergoes a similar phosphazene ring-opening polymerization at 250 °C to yield polymer **13** (Scheme III). Unlike the cyclic trimeric analogue **7**, polymer **13** reacts with piperidine with replacement of the chlorine atoms and opening of the carborane cage with concurrent formation of the piperidinium cation **14**. It is not clear why this structure is stabilized by a piperidinium cation (rather than by the phosphazene skeletal basic site as in **8**).

The structure of the polymers of type **14** was determined by a combination of microanalytical, ^{31}P NMR, and infrared techniques. First, the microanalytical data for **14** (see Experimental Section) were compatible with an approximate ratio of one carboranyl residue to five piperidino groups. Hence, the ratio of the two types of repeating units in the trimer was retained in the polymer. Second, the ^{31}P NMR spectrum showed two peaks at

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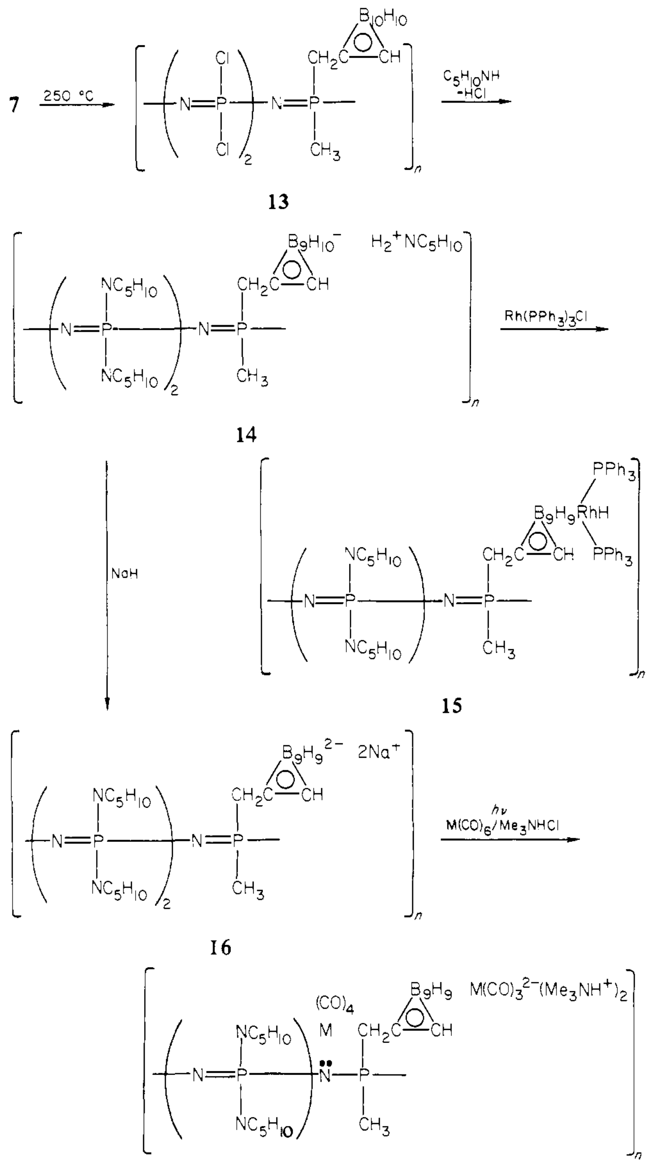
Scheme III



−9 and 14 ppm. The peak at −9 ppm was assigned to $P(NC_5H_{10})_2$ units by comparison with the similar value (−8 ppm) found for the homopolymer $[NP(NC_5H_{10})_2]_n$.[16] Thus, the peak at 14 ppm was assigned to carboranyl-PCH_3 units. The infrared spectrum of **14** was very similar to that of $[NP(NC_5H_{10})_2]_n$, with additional peaks being detected at 3190 cm^{-1} (N–H) and at 2510 cm^{-1} (B–H).

The objective of the next step was to prepare polymer-immobilized rhodium catalysts similar to those that have been described elsewhere with the use of polystyrene as a carrier.[17-20] Hence, a tetrahydrofuran solution of tris(triphenylphosphine)rhodium(I) chloride was allowed to react at 66 °C with polymer **14**. Polymer **15** was obtained. Confirmation of structure **15** was obtained from infrared and ^{31}P NMR spectra. For example, the infrared spectrum of **15** contained absorptions characteristic of triphenylphosphine (1450 cm^{-1}), carborane, and the piperidine-substituted phosphazene unit. The ^{31}P NMR spectrum of **15** contained broad resonances at 14 and −9 ppm. The peak at −9 ppm was assigned to $P(NC_5H_{10})_2$ units, and the one at 14 ppm to carboranyl PCH_3 units. Further resolution of the peaks and splitting pattern could not be accomplished, a problem associated with most polyphosphazenes.

The analogous deprotonation reaction of polymer **14** was carried out in tetrahydrofuran with sodium hydride as the reducing agent.[4] When $W(CO)_6$ or $Mo(CO)_6$ was added to two separate solutions of the sodium salt **16** at room temperature followed by exposure to ultraviolet irradiation, carbon monoxide was evolved immediately. The yellow solutions were treated separately with trimethylamine hydrochloride to precipitate polymers **17**. Characterization of polymers **17** was carried out by a combination of infrared, ^{31}P NMR spectroscopy, and microanalytical data. The infrared spectrum of **17** contained absorptions at 3250 cm^{-1} (m) (N—H), 2950 and 2850 cm^{-1} (s) (C—H), 2500 cm^{-1} (s) (B—H), 2150 (s), 2050 (w), 1990 (m), 1850 (s), 1825 (s), and 1800 (m) (C≡O), and 1260 cm^{-1} (s) (P=N). The ^{31}P NMR spectrum consisted of two broad resonances at −9 and 12 ppm. The peak at 12 ppm was assigned to carboranyl-PCH_3 units, and the one at −9 ppm was assigned to $P(NC_5H_{10})_2$. The microanalytical data suggested that, as in the case of the analogous trimer, coordination of the metal occurred to the skeletal or side-group nitrogen atoms as well as the carboranyl function. A control reaction with the poly[bis(piperidino)phosphazene] homopolymer confirmed that this species coordinates to tungsten or molybdenum carbonyls. Thus, in (metallocarboranyl)phosphazenes of these types, coordination by the skeletal or piperidino nitrogen atoms competes with coordination by the *nido*-carborane. This phenomenon may offer unusual opportunities for the design of new catalyst systems.

Catalytic Studies. The utility of compounds **10** and **15** as homogeneous hydrogenation catalysts was established in the following manner: Tetrahydrofuran solutions of **10** or **15** under a hydrogen atmosphere (2.5 atm, 25 °C) catalyzed the hydrogenation of 1-hexene. Concurrent isomerization was observed, but, at the end of 48 h, compound **10** catalyzed the conversion of essentially all of the hexenes to *n*-hexane. Similarly, in the presence of polymer **15**, complete conversion to *n*-hexane was achieved within 76 h. Compounds **10** and **15** were recovered unchanged.

Experimental Section

Materials. Benzene, piperidine, toluene, acetonitrile, and triethylamine (Fisher) were dried by distillation from calcium hydride. Ethanol (Baker) was distilled from magnesium chips. 2-Propanol (Fisher) was used as received. Tetrahydrofuran (Baker) was dried by distillation from a sodium benzophenone–ketyl slurry. $[NPCl_2]_3$ (Ethyl Corporation) was sublimed and recrystallized from hexane. Propargyl bromide, $Rh(PPh_3)_3Cl$, methyllithium (2 M in THF), and sodium hydride (50% dispersion in mineral oil) were obtained from Aldrich and were used as received. Methylmagnesium chloride (3 M in THF), $W(CO)_6$, and $Mo(CO)_6$ (Alfa) were used as received. Decaborane (Alfa) was sublimed before use.

Analytical Equipment. Infrared spectra were recorded on a Perkin-Elmer Model 580 grating spectrometer. ^{31}P NMR spectra were recorded on a JEOL PS-100 FT NMR spectrometer. Microanalyses were performed by Galbraith Labs., Inc., Knoxville, TN.

Reaction of (Methylcarboranyl)pentachlorocyclotriphosphazene or (Phenylcarboranyl)pentachlorocyclotriphosphazene (1, X = Cl, R = Me or Ph) with Piperidine To Yield 3. A solution of **1** (1.88×10^{-3} mol) in dry benzene (20 mL) was treated with piperidine (1.41×10^{-1} mol) for 28 h at 80 °C. The mixture was cooled and filtered to isolate the insoluble hydrochloride salt. Solvent was evaporated from the filtrate, and the white solid residue was washed with ethanol (100 mL). Purification of both compounds (**3**) was effected by recrystallization from toluene (mp for R = CH_3, 290 °C; for R = C_6H_5, 252 °C). Typical yields obtained for both compounds were 95%. The mass spectra of these compounds showed parent peaks at *m/e* 851 for R = C_6H_5 (M_r = 851) and at *m/e* 789 for R = CH_3 (M_r = 789). Major peaks corresponding to the successive loss of five piperidino groups were also observed.

Anal. Calcd for **3** (R = CH_3): B, 12.35; C, 50.30; H, 9.53; P, 11.81; N, 16.00. Found: B, 12.12; C, 50.45; H, 9.50; P, 11.72; N, 16.22.

Anal. Calcd for **3** (R = C_6H_5): B, 11.44; C, 53.69; H, 9.07; P, 10.95; N, 14.84. Found: B, 11.21; C, 53.84; H, 9.29; P, 10.90; N, 14.73.

Treatment of 3 with $Rh(PPh_3)_3Cl$. A solution of **3** (R = CH_3 or Ph) (3.73×10^{-3} mol), $Rh(PPh_3)_3Cl$ (3.45 g, 3.73×10^{-3} mol), and 100 mL of deoxygenated benzene/ethanol (1:1) were boiled at reflux for 12 h.

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The mixture was then cooled and filtered. Solvent was evaporated from the filtrate, and the remaining solid was recrystallized from toluene to give an almost quantitative recovery of compound **3**.

Synthesis of 1-Methyl-1-hydrido-3,3,5,5-tetrachlorocyclotriphosph(P^V)azene (5). Hexachlorocyclotriphosphazene (**4**) (5.0 g, 0.014 mol) and $[n\text{-Bu}_3\text{PCuI}]_4$ (3.0 g, 0.019 mol) were stirred together in tetrahydrofuran (150 mL) at −80 °C, and methylmagnesium chloride or bromide (10 mL of 3 M solution in THF) was added dropwise over a period of ~30 min. The temperature was allowed to rise to 25 °C, and the mixture was stirred for an additional 12 h. The mixture was then cooled to 0 °C, and 2-propanol (10 mL) was added. Finally, removal of the solvent in vacuo and sublimation of the residue gave **5** in up to 85% yield.

Synthesis of 1-Methyl-1-(2-propynyl)-3,3,5,5-tetrachlorocyclotriphosph(P^V)azene (6). 1-Methyl-1-hydridotetrachlorocyclotriphosphazene **5** (6.9 g, 0.024 mol) was dissolved in tetrahydrofuran (150 mL) and cooled to −80 °C. Methyllithium (0.019 mol, 9.5 mL of 2 M solution in THF) was added dropwise over a period of ~45 min. The mixture was stirred for an additional 30 min at −80 °C, and propargyl bromide (10 mL) was added over a period of ~30 min. The temperature was allowed to rise to 25 °C, and the mixture was stirred for an additional 12 h. Finally, removal of the solvent and recrystallization of the residue from hot hexane gave **6** in 70% yield.

Synthesis of 1-Methyl-1-[(*o*-carboranyl)methylene]-3,3,5,5-tetrachlorocyclotriphosph(P^V)azene (7). A solution of decaborane (2.8 g, 0.026 mol) in acetonitrile (30 mL) and benzene (150 mL) was boiled at reflux for 4 h. A white precipitate of bis(acetonitrile)decaborane formed. To this refluxing mixture was added 1-methyl-1-(2-propynyl)tetrachlorocyclotriphosphazene (**6**, 4.40 g, 0.013 mol) in benzene (50 mL) dropwise over a period of 1 h. The mixture was then stirred at reflux for an additional 24 h and was cooled to room temperature. Removal of the solvent and recrystallization of the residue from hot hexane gave compound **7** as white crystals in up to 90% yield, mp 186–188 °C. The mass spectrum of this compound showed a parent peak at m/e 449 ($M_r \simeq 449$), with major peaks corresponding to the successive loss of four chlorine atoms.

Anal. Calcd: B, 24.08; C, 10.70; H, 3.57; P, 20.69; N, 9.35; Cl, 31.59. Found: B, 23.94; C, 10.73; H, 3.60; P, 19.97; N, 9.19; Cl, 31.03.

Reaction of 1-Methyl-1-[(*o*-carboranyl)methylene]-3,3,5,5-tetrachlorocyclotriphosph(P^V)azene (7) with Piperidine. A solution of **7** (1.9 g, 0.0043 mol), piperidine (32 mL, 0.325 mol), and benzene (100 mL) was boiled at reflux for 12 h. The mixture was then cooled and filtered to isolate the insoluble piperidinium hydrochloride salt. Solvent was evaporated from the filtrate, and the white solid residue was washed with warm water (500 mL) to yield **8**. Compound **8** was purified further by precipitation from methylene chloride into hexane. A 95% yield of **8** was obtained; mp 283 °C. The mass spectrum of **8** showed a parent peak at m/e 635 ($M_r = 635$), with major peaks corresponding to the successive loss of four piperidine groups.

Anal. Calcd: B, 15.35; C, 45.48; H, 9.00; P, 14.69; N, 15.47. Found: B, 15.47; C, 45.40; H, 9.12; P, 14.57; N, 15.55.

Reaction of 8 with Triethylamine. A solution of **8** (3.0 g, 0.0047 mol) and triethylamine (25 mL) in acetonitrile (150 mL) was boiled at reflux for 12 h. The mixture was then cooled and filtered. Removal of the solvent and recrystallization of the residue from hot ethanol gave compound **9** in 90% yield; mp 230 °C.

Anal. Calcd: B, 13.24; C, 49.03; H, 9.81; P, 12.66; N, 15.25. Found: B, 13.34; C, 49.32; H, 9.82; P, 12.42; N, 15.01.

Reaction of 9 with $\text{Rh(PPh}_3)_3\text{Cl}$. A solution of **9** (1.0 g, 1.36×10^{-3} mol) and $\text{Rh(PPh}_3)_3\text{Cl}$ (1.2 g, 1.35×10^{-3} mol) in 150 mL of deoxygenated ethanol was boiled at reflux for 12 h. The mixture was then cooled and filtered. The filtrate was concentrated in vacuo, and the yellow powdery compound **10** was isolated on cooling.

Anal. Calcd: B, 7.71; C, 57.14; H, 6.90; P, 12.30; N, 7.78; Rh, 8.16. Found: B, 7.79; C, 57.34; H, 6.80; P, 12.15; N, 7.72; Rh, 8.10.

Reaction of Compound 8 with NaH. A solution of 1.0 g (1.57×10^{-3} mol) of **8** in tetrahydrofuran (60 mL) was added slowly to a stirred suspension of sodium hydride (0.076 g, 3.14×10^{-3} mol; 0.152 g of a 50% dispersion in mineral oil that had been washed twice with 10 mL of tetrahydrofuran) in 30 mL of the same solvent. The reaction mixture was stirred at reflux for 8 h. Stirring and heating were then stopped, and the reaction mixture was allowed to cool to room temperature. When the excess sodium hydride had settled, the clear tetrahydrofuran solution was decanted under nitrogen for use in the following reaction.

Reaction of 11 with M(CO)_6 (M = W, Mo). To two separate solutions of **11** (1.57×10^{-3} mol) in tetrahydrofuran in quartz tubes were added 3.2×10^{-3} mol of W(CO)_6 and Mo(CO)_6, respectively. The tubes were irradiated with a Hanovia Type A 350-W mercury lamp for 48 h. The solution immediately became yellow, and carbon monoxide was evolved. The yellow solutions were poured separately into 150 mL of water, and a 200% excess of aqueous trimethylamine hydrochloride was added. The precipitates were collected by filtration, dried under vacuum, and stored in vacuo (0.05 mmHg) at 25 °C to remove any unreacted metal hexacarbonyls. The products were recrystallized from solutions in mixtures of hexane and tetrahydrofuran.

Anal. Calcd for **12** (M = Mo): B, 8.53; C, 38.98; H, 6.58; O, 9.83; P, 8.10; N, 11.06; Mo, 16.85. Found: B, 8.79; C, 38.72; H, 6.27; O, 9.76; P, 8.01; N, 11.53; Mo, 16.92.

Anal. Calcd for **12** (M = W): B, 7.39; C, 33.76; H, 5.70; O, 8.52; P, 7.07; N, 9.58; W = 27.97. Found: B, 7.68; C, 33.59; H, 5.75; O, 8.13; P, 7.32; N, 9.18; W = 27.41.

Thermal Polymerization of 7. A 2-g portion of **7** was placed in a 10 × 1 cm constricted Pyrex tube. Air was removed on a vacuum line for 5 h at 0.05 torr, and the contents were subjected to a melt–freeze evacuate cycle before the tube was sealed. The tube was then encased in a wire screen jacket and was heated in a thermoregulated oven at 250 °C for 6.5 h.[16,21,22]

Synthesis of 14. A solution of 1.0 g (1.57×10^{-3} mol) of **13** in tetrahydrofuran (60 mL) was treated with piperidine (4.8×10^{-2} mol) for 24 h at 66 °C. The solution turned white immediately, with some precipitation of the polymer. An additional 70 mL of acetonitrile was added to the refluxing solution to redissolve the precipitated polymer, and the resulting solution was boiled at reflux for an additional 48 h. The granular polymer was obtained by precipitation of an acetonitrile solution of the product into water and benzene, respectively, to give **14**. Polymer **14** was stable to water and was soluble in DMF, acetonitrile, or tetrahydrofuran.

Anal. Calcd: B, 13.53; C, 48.45; H, 9.47; P, 12.95; N, 15.59. Found: B, 13.62; C, 48.52; H, 9.19; P, 12.93; N, 15.63. The GPC average molecular weight was found to be 1×10^5.

Reaction of 14 with $\text{Rh(PPh}_3)_3\text{Cl}$. **14** (0.5 g, 7.8×10^{-4} mol) and $\text{Rh(PPh}_3)_3\text{Cl}$ (0.72 g, 7.8×10^{-4} mol) were dissolved in dry, deoxygenated tetrahydrofuran (100 mL) and boiled at reflux for 24 h. The solution was cooled and concentrated, and the granular polymer **15** was obtained by precipitation into benzene. It was soluble in THF, acetonitrile, or DMF.

Reaction of 14 with NaH followed by M(CO)_6 (M = W, Mo). Two solutions of **14** (1 g, 1.56×10^{-3} mol) in 80 mL of tetrahydrofuran were added slowly to stirred suspensions of sodium hydride (3.6×10^{-3} mol) in 50 mL of the same solvent. The reaction mixtures were stirred at reflux for 12 h. The solutions were allowed to cool, and the clear tetrahydrofuran solutions were decanted under nitrogen into two separate 250-mL quartz tubes. One of the solutions was treated with Mo(CO)_6 (3.2×10^{-3} mol). The other was treated with an equimolar amount (e.g., 3.2×10^{-3} mol) of W(CO)_6, and both solutions were irradiated with a Hanovia Type A 350-W mercury lamp for 48 h. The solutions turned yellow immediately, with evolution of carbon monoxide. The reaction mixtures were treated with a 200% excess of aqueous trimethylamine hydrochloride to precipitate the polymers of type **17**. The granular polymers were collected by filtration, dried under vacuum, and stored in vacuum (0.05 torr) at 25 °C to remove any free metal hexacarbonyls.

Hydrogenation Experiments. Separate solutions of **9**, **10**, **14**, **15**, and $\text{Rh(Cl)(PPh}_3)_3$ (10^{-3} mol trimer units) in dry, deoxygenated THF (30 mL) with 1-hexene (10^{-1} mol) were pressurized with H_2 (2.5 atm) and were shaken at 25 °C. The progress of each reaction was interrupted periodically to remove and vacuum distill samples for vapor-phase chromatography analysis. As would be expected, the metal-free compounds **9** and **14** showed no catalytic activity. $\text{Rh(Cl)(PPh}_3)_3$ induced a rapid hydrogenation that was essentially complete in minutes. When compound **10** was present, the hydrogenation was over 98% complete in 48 h. Compound **15** brought about complete hydrogenation in 76 h.

X-ray Data Collection and Structure Solution. A colorless, paralleliped crystal of **8**, of approximate dimensions 0.27 × 0.33 × 0.42 mm, was mounted on a glass fiber with the longest dimension coincident with the fiber axis. Least-squares refinement of 25 reflections indicated a monoclinic cell of dimensions a = 11.199 (3), b = 17.924 (5), and c = 18.163 (16) Å, β = 92.29 (4)°, and V = 3643 (5) Å, with Z = 4, d_{calcd} = 1.16 g cm^{-3}. Inspection of a small test data set (axial and zero-layer reflections) indicated the space group of $P2_1/n$ (No. 14, C_{2h}^5).[23] Intensity data were measured for 5884 reflections ($3.0 < 2\theta < 47.0°$) with Mo Kα radiation with an Enraf-Nonius CAD 4 diffractometer equipped with a graphite single-crystal monochromator. From these, 3036 unique observed reflections ($I > 2\sigma(I)$) were obtained. Other conditions of the data collection were as follows: scan range (0.7 + 0.347 tan θ) below and above the calculated Kα_1 and Kα_2 reflections; scan rate, 1.0–5.0° min^{-1};

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J. Am. Chem. Soc. **1983**, *105*, 1321-1327 1321

three standard reflections measured every 60 min; drift corrections (from standards), 1.092-1.006. No absorption corrections were applied (μ = 0.194 mm^{-1}) because Ψ scans suggested that the absorption was not severe.

All atoms including H atoms were located from Patterson and electron-density synthesis.[24] In the final cycles of least-squares refinement, 391 parameters were refined, including positional and anisotropic thermal parameters[25] for all non-hydrogen atoms. The hydrogen atoms were placed at positions that gave the closest agreement with the peaks found in difference Fourier maps (C-H = 0.97 Å, B-H = 0.97 Å), except for H9, which was positioned at the location found from a difference map. In the last cycle of refinement, one parameter [H2N, x coordinate] shifted by 1.6 σ, and another [H2N, y coordinate] shifted by 1.1 σ; the largest shift of all other atoms was 0.07 σ. Convergence was achieved with R = 0.077 and R_w = 0.070.[26] The highest peak on the final difference electron-density map (0.19 e Å^{-3}) was located between C54 and C55 of a piperidino side group. Complex scattering factors, corrected for anomalous dispersion, were used.[27]

Acknowledgment. This work was supported by a grant from NASA Ames Research Center.

Registry No. 1 (X = Cl; R = Me), 74721-85-0; **1** (X = Cl; R = Ph), 74721-87-2; **3** (R = Me), 84393-75-9; **3** (R = Ph), 84393-77-1; **4**, 940-71-6; **5**, 68351-74-6; **6**, 77217-45-9; **7**, 84254-25-1; **8**, 84393-78-2; **9**, 84393-79-3; **10**, 84416-56-8; **11**, 84369-00-6; **12** (M = Mo), 84416-58-0; **12** (M = W), 84416-60-4; **13** polymer, 84254-26-2; **13** repeating unit, 84254-27-3; **14**, 84332-49-0; **15**, 84393-80-6; **17** (M = Mo), 84393-82-8; **17** (M = W), 84393-84-0; $Rh(PPh_3)_3Cl$, 14694-95-2; [n-Bu_3PCuI]$_4$, 59245-99-7; $Rh(H)(PPh_3)_3$, 16973-49-2; $W(CO)_6$, 14040-11-0; $Mo(CO)_6$, 13939-06-5; NaH, 7646-69-7; 1-hexene, 592-41-6; *n*-hexane, 110-54-3; piperidine, 110-89-4; methylmagnesium chloride, 676-58-4; methylmagnesium bromide, 75-16-1; propargyl bromide, 106-96-7; decaborane, 17702-41-9; triethylamine, 121-44-8.

Supplementary Material Available: Tables of observed and calculated structure factors, positional and thermal parameters, and bond length and angles for **8** (22 pages). Ordering information is given on any current masthead page.

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(24) All programs used in data collection reduction and refinement are part of the Enraf-Nonius Structure Determination Package, Enraf-Nonius, Delft, The Netherlands, 1975 (revised 1977).

(25) Anisotropic thermal parameters are of the form $\exp(-2\pi^2(U_{11}h^2(a^*)^2 + ... + 2U_{23}klb^*c^*))$. Isotropic thermal parameters are of the form $\exp(-B(\sin^2\theta)/\pi^2)$.

(26) $R = \sum(||F_o| - |F_c||)/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$; $\sum w = 1/\sigma(F_o)^2$.

(27) "International Tables for X-ray Crystallography", 3rd ed.; Kynoch Press: Birmingham, England, 1968; Vol. III.

Iron- and Ruthenium-Linked Phosphazenes[1]

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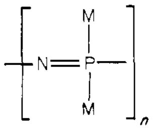
Abstract: A series of new organometallic phosphazenes that contains Fe-P, Ru-P, Ru-Ru, and Fe-Ru bonds has been isolated. The anions $[Fe(CO)_2Cp]^-$ and $[Ru(CO)_2Cp]^-$ react with $(NPF_2)_3$ (**2**) to replace first one and then two (geminal) fluorine atoms by $M(CO)_2Cp$ groups. The monoruthenium derivative (**5**) reacts with $[Fe(CO)_2Cp]^-$ to form a geminal, mixed-metal organometallic phosphazene (**7**) that, on photolysis, undergoes decarbonylation to an Fe-Ru bonded derivative (**8**). The monoiron cyclotriphosphazene (**9**) does not yield the same mixed-metal species when treated with $[Ru(CO)_2Cp]^-$ but instead forms the new mixed-metal dimer, $FeRu(CO)_4Cp_2$ (**10**). This dimer can also be prepared by the reaction of $[Ru(CO)_2Cp]^-$ with $Fe(CO)_2CpI$. Species **8** and its diiron analogue, **4**, undergo metal-metal bond cleavage with carbon monoxide. Species **7** and **8** are the first examples of phosphazenes with two different metals linked to a phosphazene ring. The new compounds were characterized by ^{31}P, ^{19}F, and ^1H NMR, infrared, and mass spectral techniques. In addition, an X-ray crystal structure analysis of the mixed-metal phosphazene **8** was carried out. The Fe-Ru bond distance in **8** is 2.698 (1) Å and the Fe-P-Ru bond angle is 73.93 (2)°. Evidence was obtained that the organometallic unit perturbs the structure of the phosphazene ring.

Our long-range objective is the synthesis of inorganic high polymers of type **1**, in which transition-metal organometallic units



$$\left[-N=\overset{\overset{M}{|}}{\underset{\underset{M}{|}}{P}}- \right]_n$$

1

(M) form the side groups covalently attached to a long phosphazene chain. If such macromolecules could be synthesized, they would be of considerable interest as prospective polymeric catalysts or electroactive materials.

The synthesis of high polymers of type **1** is a complex undertaking. Until recently[2-4] no reactions were known that would link transition metals to phosphazenes through a P-M covalent bond. Moreover, the realities of polymer synthesis require that species such as **1** must be prepared either by the ring-opening polymerization of cyclic oligomeric analogues[5] or by substitution reactions carried out on a preformed macromolecular chain.[6] In either case, the first step is the development of procedures at the small-molecule level that would permit a wide range of metals to be linked to a phosphazene ring. If the polymer substitution route to **1** is later preferred, these small-molecule reactions will function as models for the macromolecular interactions.[7]

Recently we reported the synthesis and molecular structure determination of two small-molecule phosphazenes (**3** and **4**) that contain phosphorus-iron bonds.[2,3] These are prototypes for a wide range of similar derivatives that contain other transition metals.

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(1) This work was presented, in part, at the 182nd National Meeting of the American Chemical Society, New York, Aug 23-28, 1981. This paper is part of a series on phosphorus-nitrogen ring systems and high polymers.

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