77827-39-5; [(*m*-xyl)(MeNEthi)$_2$Me$_2$[16]tetraene](ZnCl$_4$)$_2$, 77827-41-9; [(*m*-xyl)(NHEthi)$_2$Me$_2$[16]tetraene](ZnCl$_4$)$_2$, 77827-42-0; [(*m*-xyl)(NHEthi)$_2$Me$_2$[16]tetraene](PF$_6$)$_3$, 77826-03-0; [(*p*-xyl)(NHEthi)$_2$Me$_2$[16]tetraene](PF$_6$)$_3$, 77826-05-2; [Ni((*p*-xyl)(MeNEthi)$_2$Me$_2$[16]tetraeneN$_4$)](PF$_6$)$_2$, 77827-44-2; [(CH$_2$)$_6$(MeNEthi)$_2$Me$_2$[16]tetraene](PF$_6$)$_3$, 76863-25-7; [(CH$_2$)$_4$(MeNEthi)$_2$Me$_2$[16]tetraene](PF$_6$)$_3$, 77826-07-4; [(CH$_2$)$_5$(MeNEthi)$_2$Me$_2$[16]tetraene](PF$_6$)$_3$, 77846-61-8; [H$_3$(CH$_2$)$_6$(MeNEthi)$_2$Me$_2$[15]tetraeneN$_4$](PF$_6$)$_3$, 77846-63-0; [Ni((CH$_2$)$_4$(MeNEthi)$_2$Me$_2$[16]tetraeneN$_4$)](PF$_6$)$_2$, 76800-64-1; [Ni((CH$_2$)$_5$(MeNEthi)$_2$Me$_2$[16]tetraeneN$_4$)](PF$_6$)$_2$, 76791-39-4; [Ni((CH$_2$)$_6$(MeNEthi)$_2$Me[16]tetraeneN$_4$)](PF$_6$)$_2$, 73914-16-6; [Ni((CH$_2$)$_7$(MeNEthi)$_2$Me[16]tetraeneN$_4$)](PF$_6$)$_2$, 76791-37-2; [Ni((CH$_2$)$_8$(MeNEthi)$_2$Me[16]tetraeneN$_4$)](PF$_6$)$_2$, 76791-41-8; [Ni((MeOEthi)$_2$Me$_2$[16]tetraeneN$_4$)](PF$_6$)$_2$, 70021-28-2; [Ni((MeNHEthi)$_2$Me$_2$[16]tetraeneN$_4$)](PF$_6$)$_2$, 74466-02-7; [Ni((*n*-BuNHEthi)$_2$Me$_2$[16]tetraeneN$_4$)]I$_2$, 77880-78-5; [Ni((BZNHEthi)$_2$Me$_2$[16]tetraeneN$_4$)]I$_2$, 77880-79-6; 1,4-diaminobutane, 110-60-1; 1,5-diaminopentane, 462-94-2; 1,6-hexanediamine, 124-09-4; NH$_2$(CH$_2$)$_7$NHz, 646-19-5; NH$_2$(CH$_2$)$_8$NH$_2$, 373-44-4; 9,9-bis(3-aminopropyl)fluorene, 2409-19-0; 9,9-bis(3-aminopropyl)fluorene dihydrochloride, 23328-59-8; *m*-xylylenediamine, 1477-55-0; *p*-xylylenediamine dihydrochloride, 51964-30-8; α,α′-dibromo-*m*-xylene, 626-15-3; α,α′-dibromo-*p*-xylene, 623-24-5.

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Synthesis of New 1-Halo-1-alkyltetrachlorocyclotriphosphazenes, Including the First Cyclophosphazenes with a P–I Bond[1]

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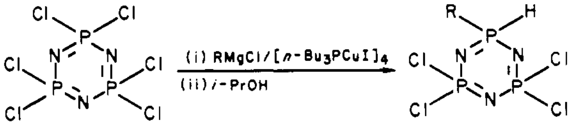
The syntheses of the first series of 1-halo-1-alkyltetrachlorocyclotriphosphazenes [halogen X = Cl (III), X = Br (IV), X = I (V)] are described, together with the structural characterization of these compounds. Compounds of type III are polymer precursors. Species of type V are the first examples of phosphazenes with a phosphorus–iodine bond. Surprisingly, the substitution reactions of these compounds with organic nucleophiles take place at a position geminal to the alkyl group.

Investigations into the chemistry of new cyclic phosphazenes are important for a number of reasons.[2,3] Small ring phosphazenes are of interest as "monomers" for the synthesis of new macromolecules,[4,5] as models for the reactions of high polymeric phosphazenes,[2,5] as polymerization initiators and mechanistic probes, and for studies related to the bonding within the phosphazene skeleton.[6]

In a recent paper[7,8] we described the synthesis of a new series of air- and moisture-sensitive cyclic phosphazenes (II) which contained a phosphorus–hydrogen bond. These compounds were synthesized via the reaction of hexachlorocyclotriphosphazene (I) with alkyl Grignard reagents in the presence of [*n*-Bu$_3$PCuI]$_4$, followed by treatment of the reaction intermediate with isopropyl alcohol.[8]



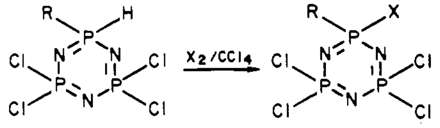
I

II

The principal objectives of this present work were to answer the following questions. (1) Can the hydrogen atom bound to phosphorus in compound II (the apparent cause of the air and moisture instability of these molecules) be replaced by chlorine to yield monoalkylpentachlorocyclotriphosphazenes? These compounds are inaccessible by other routes. (2) Could other halogen atoms (such as bromine or iodine) be attached to the phosphazene ring via replacement of the hydrogen atom in compounds II, and, if so, what would be the air or moisture sensitivity and thermal stability of these new mixed halophosphazenes? And, finally, (3) how would the presence of the different halogen atoms on the phosphazene ring affect the reactivities of these compounds?

Results and Discussion

The Synthesis Reaction. When hydridophosphazenes (II)



II

III, X = Cl
IV, X = Br
V, X = I

were allowed to react with an excess of halogen (chlorine, bromine, or iodine) in tetrachloromethane, the hydrogen atom was replaced cleanly and smoothly by the halogen to yield a new class of 1-halo-1-alkyltetrachlorocyclotriphosphazenes (III, IV, or V). These compounds possess an alkyl group and the added halogen atom (chlorine, bromine, or iodine) linked to the same phosphorus atom. The range of compounds III–V, where R = CH$_3$, C$_2$H$_5$, *n*-C$_3$H$_7$, *n*-C$_4$H$_9$, *i*-C$_3$H$_7$, and *t*-C$_4$H$_9$, were prepared.

General Characteristics of Alkylpentachlorocyclotriphosphazenes, N$_3$P$_3$Cl$_5$R (III). The reaction of hydridophosphazenes (II) with elemental chlorine provides the most effective general synthetic route for the formation of alkylpentachlorocyclotriphosphazenes (III). All these compounds are air- and moisture-stable, volatile products. Where R = CH$_3$, C$_2$H$_5$, or *n*-C$_3$H$_7$, they are white crystalline compounds. When R = *i*-C$_3$H$_7$, *n*-C$_4$H$_9$, or *t*-C$_4$H$_9$, they are colorless oils at 25 °C. In a recent paper[4,5] we have shown that these monoalkylpentachlorocyclotriphosphazenes (III) are "monomers" for the formation of a new class of high molecular weight poly(organophosphazenes) which contain phosphorus–carbon bonds.

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(1) For a previous paper in this series see: Allcock, H. R.; Greigger, P. P.; Wagner, L. J.; Bernheim, M. Y. *Inorg. Chem.* **1981**, *20*, 716.
(2) Allcock, H. R. *Acc. Chem. Res.* **1979**, *12*, 351.
(3) Allcock, H. R. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 147.
(4) Ritchie, R. J.; Harris, P. J.; Allcock, H. R. *Macromolecules*, **1979**, *12*, 1014.
(5) Allcock, H. R.; Ritchie, R. J.; Harris, P. J. *Macromolecules*, **1980**, *13*, 1332.
(6) Ritchie, R. J.; Harris, P. J.; Allcock, H. R. *Inorg. Chem.* **1980**, *19*, 2483.
(7) Harris, P. J.; Allcock, H. R. *J. Am. Chem. Soc.* **1978**, *100*, 6512.
(8) Allcock, H. R.; Harris, P. J. *J. Am. Chem. Soc.* **1979**, *101*, 6221.

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Characteristics of 1-Alkyl-1-bromotetrachlorocyclotriphosphazenes, $N_3P_3Cl_4BrR$ (IV). Compounds of type IV represent the first series of 1-alkyl-1-bromotetrachlorocyclotriphosphazenes to be synthesized. These compounds, like species III discussed previously, are air- and moisture-stable, volatile products. Compounds of type IV where R represents a linear alkyl group (CH_3, C_2H_5, n-C_3H_7, n-C_4H_9) are white, crystalline products. Compounds of type IV in which R represents a branched alkyl group (i-C_3H_7, t-C_4H_9) are colorless oils. The air and moisture stability of these compounds is surprising in view of the fact that the phosphorus–bromine bond in many compounds is known to hydrolyze rapidly in moist air. Work is at present under way in our laboratory to explore the possibility that these bromophosphazene compounds might function as catalysts for the polymerization of hexachlorocyclotriphosphazene.[3,9]

Characteristics of 1-Alkyl-1-iodotetrachlorocyclotriphosphazenes, $N_3P_3Cl_4IR$ (V). Compounds of type V represent the first series of cyclophosphazene compounds to be synthesized that contain a phosphorus–iodine bond. Compounds of type V with R = CH_3, C_2H_5, n-C_3H_7, or n-C_4H_9 are white, volatile, crystalline products. Compounds of type V with R = i-C_3H_7, t-C_4H_9 are colorless oils. Many of these iodophosphazene compounds were found to have a relatively low thermal stability. Species V (R = CH_3, C_2H_5, n-C_3H_7) could be sublimed (100 °C (0.1 mmHg)) with only slight decomposition. However, all the other iodophosphazenes decomposed if heated in vacuo to temperatures above 80 °C. An interesting feature of all the iodophosphazene compounds of type V is their relatively high stability to air and moisture. Species V (R = CH_3, C_2H_5) decomposed slowly over a period of days when exposed to the atmosphere, whereas compounds of type V (R = n-C_3H_7, n-C_4H_9, i-C_3H_7, t-C_4H_9) withstood exposure to the atmosphere for a period of weeks without extensive decomposition.

Structure Proof for Species III–V. All the 1-alkyl-1-halotetrachlorocyclotriphosphazenes (III–V) synthesized in this study were characterized by infrared and ^1H and ^{31}P NMR spectroscopy, mass spectrometry (low and high resolution) and, in representative cases, elemental analysis. These data are listed in Tables I, II, and III. Tables II and III are available as supplementary material.

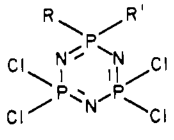
The compounds of type III yielded a strong parent ion in the mass spectrum, with a characteristic Cl_5 isotope pattern. Species IV gave a moderately intense parent ion in the mass spectrum, with a characteristic Cl_4Br isotope pattern. Compounds of type V displayed a barely discernible parent ion under electron impact mass spectrometric conditions. However, chemical ionization mass spectral analysis of these compounds (with use of methane as a carrier gas) revealed a strong parent ion (plus proton), with a characteristic Cl_4 isotope pattern. A detailed description of the fragmentation pathways of these compounds will be presented elsewhere.

The presence of the phosphazene ring in compounds III–V was confirmed by the use of a combination of infrared and ^{31}P NMR spectroscopy. The infrared spectra of all the compounds (listed in Table II) contained an intense absorbance between 1100 and 1300 cm^{-1}, a characteristic of the P=N skeleton in cyclotriphosphazenes.[3] Other bands in these spectra could be assigned to C–H and P–Cl vibrations.[10,11]

The ^{31}P NMR spectra of species III–V (listed in Table III) could be interpreted as simple AB_2 spin systems.[12] However, all spectral lines were broadened by $\simeq$2 Hz due to quadrupole coupling to ring nitrogen atoms. The position of resonance for two magnetically equivalent PCl_2 units in each compound always appeared as a doublet, centered at $\simeq$21 ppm. This resonance position was apparently independent of the nature of the other substituents on the phosphazene ring. The resonance for the phosphorus atom bound to the alkyl group and the added halogen atom always appeared as a triplet. The chemical shift displayed certain trends that were apparently dependent on the nature of the substituents. Within each series of compounds III–V, the position of resonance for this phosphorus atom was found to move downfield with the increasing electron-donating ability of the alkyl group. This effect has been observed in other phosphorus[13,14] and phosphazene[15] compounds. Comparison of a series of compounds III–V which contain the same alkyl group showed that the position of resonance for the substituted phosphorus moved to a higher field (more shielded) with increasing size of the halogen atom. This trend is also observed in many phosphorus compounds, and, in general, the phosphorus resonance for P–I compounds appears upfield from that found for the corresponding P–Cl compound.[14]

The alkyl side group in compounds III–V could be identified by inspection of the ^1H NMR spectra of these compounds. These data are also listed in Table III. Each alkyl group gave rise to a characteristic pattern of resonances. High-resolution ^1H NMR spectra (200 MHz) and ^{31}P decoupled ^1H NMR spectra (100 MHz), recorded for the series of compounds III, allowed the assignment of every proton chemical shift and the determination of every coupling constant to be made for this series.

Reactivity of Species III–V. The reactions of compounds III–V (R = CH_3) with various oxygen and nitrogen nucleophiles were investigated. These reactions were carried out in order to determine if compounds III–V would show different reactivities depending on the nature of the halogen atom, X. Compounds III, IV, or V (R = CH_3) were treated with 1 equiv of the nucleophiles, NaOMe and NaOPh, and 2 equiv of the amines, n-$BuNH_2$ or t-$BuNH_2$ (1 equiv of the amine was required as an HCl acceptor). These particular reagents were chosen because they are known to follow different substitution pathways when allowed to react with $(NPCl_2)_3$.[3,16–19] This variation in reactivity has been used as evidence for the existence of S_N1 or S_N2 reaction mechanisms.[3] However, all the reactions examined in this study resulted in the exclusive formation of the *geminally* substituted products, VI. These



VI

R' = n-BuNH
= t-BuNH
= OMe
= OPh

organo-substituted derivatives were characterized by a combination of infrared and ^1H and ^{31}P NMR spectroscopy and mass spectrometry (low and high resolution). These data are

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(9) Allcock, H. R.; Best, R. J. *Can. J. Chem.* **1964**, *42*, 447.
(10) Corbridge, D. E. C. *J. Appl. Chem.* **1956**, *6*, 456.
(11) Colthup, N. B.; Daley, L. H.; Wiberley, S. E. "Introduction to Infrared and Raman Spectroscopy"; Academic Press: New York, 1975.
(12) Bovey, F. A. "Nuclear Magnetic Resonance Spectroscopy"; Academic Press: New York, 1969.
(13) Grim, S. O.; McFarlane, W.; Davidoff, E. F.; Martes, T. J. *J. Phys. Chem.* **1966**, *70*, 587.
(14) Letcher, J. H.; Van Wazer, J. R. *Top. Phosphorus Chem.* **1967**, *5*, 75.
(15) Allcock, H. R.; Harris, P. J.; Connolly, M. S. *Inorg. Chem.* **1981**, *20*, 11.
(16) Fitzsimmons, B. W.; Hewlett, C.; Hills, K.; Shaw, R. A. *J. Chem. Soc. A* **1967**, 679.
(17) Dell, D.; Fitzsimmons, B. W.; Keat, R.; Shaw, R. A. *J. Chem. Soc. A* **1966**, 1680.
(18) Ray, S. K.; Shaw, R. A.; Smith, B. C. *J. Chem. Soc.* **1963**, 3236.
(19) Feakins, D.; Nabi, S. N.; Shaw, R. A.; Watson, P. *J. Chem. Soc. A* **1968**, 10.

Table I. Haloalkylphosphazenes: Characterization Data

			mass spectral data[21]		elemental anal.[21,22]	
compd	% yield	mp, °C	found	calcd	found	calcd
$N_3P_3Cl_5(CH_3)$	92	125-126	325	325	C 3.73	C 3.66
					H 0.99	H 0.92
					N 12.80	N 12.82
					P 28.55	P 28.40
					Cl 54.08	Cl 54.19
$N_3P_3Cl_5(C_2H_5)$	90	41-42	339	339	C 7.18	C 7.03
					H 1.61	H 1.46
					N 12.26	N 12.30
					P 27.11	P 27.23
					Cl 52.03	Cl 51.98
$N_3P_3Cl_5(n\text{-}C_3H_7)$	92	50-52	353	353	C 10.21	C 10.13
					H 2.06	H 1.97
					N 11.94	N 11.81
					P 25.99	P 26.16
					Cl 49.84	Cl 49.93
$N_3P_3Cl_5(n\text{-}C_4H_9)$	86	oil	367	367	C 12.91	C 13.01
					H 2.50	H 2.50
					N 11.17	N 11.37
					P 24.95	P 25.16
					Cl 48.09	Cl 48.01
$N_3P_3Cl_5(i\text{-}C_3H_7)$	74	oil	353	353	C 10.09	C 10.13
					H 1.95	H 1.97
					N 11.66	N 11.81
					P 26.80	P 26.16
					Cl 49.71	Cl 49.93
$N_3P_3Cl_5(t\text{-}C_4H_9)$	66	oil	367	367	C 13.25	C 13.01
					H 2.56	H 2.44
					N 11.41	N 11.37
					P 24.95	P 25.16
					Cl 48.21	Cl 48.01
$N_3P_3Cl_4Br(CH_3)$	85	122-123	369	369	C 3.16	C 3.22
					H 0.75	H 0.81
					N 11.22	N 11.29
					P 25.19	P 25.00
					Cl 38.22	Cl 38.17
					Br 21.76	Br 21.51
$N_3P_3Cl_4I(CH_3)$	81	94-95	417	417	C 2.90	C 2.86
					H 0.70	H 0.71
					N 9.91	N 10.02
					P 22.08	P 22.19
					Cl 34.04	Cl 33.89
					I 30.18	I 30.81
$N_3P_3Cl_4I(C_2H_5)$	78	86-87	431	431	C 5.76	C 5.54
					H 1.15	H 1.15
					N 9.98	N 9.69
					P 21.64	P 21.47
					Cl 32.54	Cl 32.79
					I 28.96	I 29.33
$N_3P_3Cl_4I(n\text{-}C_3H_7)$	72	94-95	445	445	C 7.97	C 8.05
					H 1.51	H 1.56
					N 9.38	N 9.39
					P 20.44	P 20.80
					Cl 30.91	Cl 31.76
					I 28.31	I 28.41
$N_3P_3Cl_4I(n\text{-}C_4H_9)$	69	49-50	459	459	C 10.38	C 10.41
					H 1.91	H 1.95
					N 9.02	N 9.11
					P 19.69	P 20.17
					Cl 30.51	Cl 30.80
					I 27.45	I 27.54
$N_3P_3Cl_4I(i\text{-}C_3H_7)$	71	oil	445	445	C 8.01	C 8.05
					H 1.48	H 1.56
					N 9.41	N 9.39
					P 20.01	P 20.80
					Cl 31.08	Cl 31.76
					I 28.23	I 28.41
$N_3P_3Cl_4I(t\text{-}C_4H_9)$	60	oil	459	459	C 10.53	C 10.41
					H 2.02	H 1.95
					N 8.99	N 9.11
					P 20.02	P 20.17
					Cl 31.09	Cl 30.80
					I 27.90	I 27.54

Table I (*Continued*)

compd	% yield	mp, °C	mass spectral data[21] found	mass spectral data[21] calcd	mol wt found	mol wt calcd
$N_3P_3Cl_4Br(C_2H_5)$	87	68-70	383	383	382.7640	382.7633
$N_3P_3Cl_4Br(n\text{-}C_3H_7)$	80	67-68	397	397	396.7802	396.7789
$N_3P_3Cl_4Br(n\text{-}C_4H_9)$	81	33-35	411	411	410.7930	410.7945
$N_3P_3Cl_4Br(i\text{-}C_3H_7)$	69	oil	397	397	396.7767	396.7789
$N_3P_3Cl_4Br(t\text{-}C_4H_9)$	60	oil	411	411	410.7928	410.7945
$N_3P_3Cl_4(OCH_3)CH_3$	85	57-59	321	321	320.8468	320.8475
$N_3P_3Cl_4(OC_6H_5)CH_3$	82	95-97	383	383	382.8633	382.8631
$N_3P_3Cl_4(n\text{-}C_4H_9NH)CH_3$	73	42-44	362	362	361.9095	365.9104
$N_3P_3Cl_4(t\text{-}C_4H_9NH)CH_3$	78	107-108	362	362	361.9111	361.9104

also listed in Tables I–III. The geminal structure of species VI was clearly demonstrated by the AB_2 spin system[12] observed in the ^{31}P NMR spectrum of these compounds. The presence of the alkoxy, aryloxy, or amino substituent was also confirmed from observation of the ^1H NMR spectra of these products. Integration of the areas under the various resonances confirmed the substituted ratio. All the compounds of structure VI displayed a strong parent peak in the mass spectrum, with a characteristic Cl_4 isotope pattern. The results of these reactions of compounds III–V ($R = CH_3$) with nucleophiles suggest that the substitution patterns of the 1-halo-1-alkyltetrachlorocyclotriphosphazenes are dominated by the influence of the organic group and apparently are unaffected by the type of halogen atom bound to the alkylated phosphorus center.

Experimental Section

Materials. Hexachlorocyclotriphosphazene (I) was kindly supplied by Ethyl Corp. and was purified by sublimation, followed by two recrystallizations from 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 ketyl drying agent. Tetrachloromethane was distilled into the reaction flask under an atmosphere of dry nitrogen from phosphorus pentoxide, used as a drying agent. The reagent $[n\text{-}Bu_3PCuI]_4$ was prepared by standard methods.[20]

Synthesis of Hydridophosphazenes (II). The syntheses of all the hydridophosphazenes (II) were carried out as described previously,[7,8] with the following modification. Hexachlorocyclotriphosphazene (I) (5.0 g, 0.014 mol) and $[n\text{-}Bu_3PCuI]_4$ (3.0 g, 0.0019 mol) were stirred together in tetrahydrofuran (THF) (150 mL) at −80 °C, and the Grignard reagent (25 mL, 3.0 M solution in THF) was added dropwise over a period of ≃30 min. 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 isopropyl alcohol (10 mL) was added. Finally, removal of the solvent in vacuo and sublimation (or distillation) of the residue gave the hydridophosphazenes (II) in high yield.

Reaction of Hydridophosphazenes (II) with Chlorine. All these reactions were carried out in an identical manner. The following is a typical procedure: Methylhydridotetrachlorocyclotriphosphazene (5.0 g, 0.017 mol) was dissolved in tetrachloromethane (150 mL) and cooled to 0 °C. Chlorine gas was then bubbled through the solution for 5 min. The reaction mixture was stirred for 1 h, after which time chlorine gas was again bubbled through the solution for a further 5 min. The mixture was stirred for a further 4 h, and the solvent and excess chlorine were then removed under vacuum. The product was then dissolved in CH_2Cl_2 and was filtered through neutral alumina to leave $N_3P_3Cl_5CH_3$ as white crystals in 92% yield (5.1 g).

Reaction of Hydridophosphazenes (II) with Bromine. All these reactions were carried out in the same manner; the following procedure is typical. Methylhydridotetrachlorocyclotriphosphazene (5.0 g, 0.017 mol) was dissolved in tetrachloromethane (150 mL) and was cooled to 0 °C. Excess bromine (3 mL) was then added to the solution, and the mixture was stirred for 8 h. The excess bromine and solvent were then removed under vacuum, and the products were extracted with dichloromethane. This solution was filtered through neutral alumina to leave the product $N_3P_3Cl_4BrCH_3$ as white crystals in 85% yield (5.4 g).

Reaction of Hydridophosphazenes (II) with Iodine. All these reactions were carried out in the same manner; the following is a typical procedure. Methylhydridocyclotriphosphazene (5.0 g, 0.017 mol) was dissolved in tetrachloromethane (150 mL) and was cooled to −20 °C. Iodine (10 g, 0.039 mol) was then added, and the mixture was stirred for 16 h during which time the temperature was allowed to rise to 25 °C. The solvent was then removed under vacuum, and the products were extracted with hexane. The crude product was purified in one of two ways: (1) compounds of type V with $R = CH_3$, C_2H_5, $n\text{-}C_3H_7$ were sublimed at 100 °C (0.1 torr) to yield the product as white crystals; (2) compounds of type V with $R = n\text{-}C_4H_9$, $i\text{-}C_3H_7$, $t\text{-}C_4H_9$ were dissolved in methylene chloride and filtered through neutral alumina, and the solvent was evaporated to leave the product as white crystals or as a colorless oil.

Reaction of Compounds III–V with $NaOCH_3$ or $NaOC_6H_5$. All these reactions were carried out in an identical manner. The following procedure is typical. Sodium methoxide or sodium phenoxide [made from sodium (0.35 g, 0.015 mol) and the alcohol or phenol (0.015 mol) in tetrahydrofuran (50 mL)] was added dropwise to a solution of the 1-alkyl-1-halotetrachlorocyclotriphosphazene III–V ($R = CH_3$) (0.015 mol) in tetrahydrofuran (150 mL) at 0 °C. The mixture was stirred for 16 h, and the temperature was allowed to rise to 25 °C. The solvent was then removed under vacuum, and the product was dissolved in methylene chloride. The crude product was purified by filtration through neutral alumina, followed by recrystallization from hexane.

Reaction of Compounds III–V with $n\text{-}BuNH_2$ or $t\text{-}BuNH_2$. These reactions were carried out in a similar manner; the following procedure is typical. The amine (2.23 g, 0.03 mol) (freshly distilled from CaH_2), dissolved in tetrahydrofuran (50 mL), was added dropwise to a solution of the 1-alkyl-1-halotetrachlorocyclotriphosphazene (0.015 mol) in tetrahydrofuran (150 mL) at a temperature of 0 °C. The mixture was stirred for 16 h, and the temperature was allowed to rise to 25 °C. The product was isolated by removal of the solvent under vacuum, followed by extraction with hexane. The products were purified by dissolving in CH_2Cl_2, followed by filtration through neutral alumina and recrystallization from hexane.

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Registry No. II, $R = CH_3$, 68351-74-6; II, $R = C_2H_5$, 71982-84-8; II, $R = n\text{-}C_3H_7$, 71982-85-9; II, $R = n\text{-}C_4H_9$, 71982-87-1; II, $R = i\text{-}C_3H_7$, 71982-86-0; II, $R = t\text{-}C_4H_9$, 71982-89-3; III, $R = CH_3$,

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(20) Kaufman, G. B.; Teter, L. A. *Inorg. Synth.* **1963**, *7*, 9.

(21) Mass spectral data were recorded with the use of an AEI-MS 902 mass spectrometer: for compounds of type III, masses were calculated by using $^{35}Cl_5$; for compounds of type IV, masses were calculated by using $^{35}Cl_4$, $^{79}Br_1$; for compounds V, masses were calculated by using $^{35}Cl_4$.

(22) Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN 37921.

(23) Infrared spectra were recorded on a Perkin-Elmer 580 infrared spectrometer. The samples were prepared as KBr disks.

(24) ^{31}P NMR spectra were recorded on a JEOL-PS 100 spectrometer operating at 40 MHz in the Fourier Transform mode. The data were processed on a Nicolet 1080 computer. All spectra were recorded on a solution of the compound in $CDCl_3$. Positive chemical shifts are downfield from external H_3PO_4.

(25) ^1H NMR spectra were recorded with the use of either a JEOL JNM-PS 100 spectrometer operating at 100 MHz (with broad-band phosphorus decoupling) or a Bruker WP-200 spectrometer operating at 200 MHz. All ^1H NMR spectra were recorded on a solution of the compound in $CDCl_3$. Chemical shifts are related to tetramethylsilane at δ 0.

(26) No attempts were made to determine the absolute sign of the coupling constants.

71332-21-3; III, R = C_2H_5, 71332-23-5; III, R = n-C_3H_7, 75132-80-8; III, R = n-C_4H_9, 75132-82-0; III, R = i-C_3H_7, 75155-05-4; III, R = t-C_4H_9, 75155-06-5; IV, R = CH_3, 77589-25-4; IV, R = C_2H_5, 77589-26-5; IV, R = n-C_3H_7, 77589-27-6; IV, R = n-C_4H_9, 77611-13-3; IV, R = i-C_3H_7, 77589-28-7; IV, R = t-C_4H_9, 77589-29-8; V, R = CH_3, 77589-30-1; V, R = C_2H_5, 77589-31-2; V, R = n-C_3H_7, 77589-32-3; V, R = n-C_4H_9, 77589-33-4; V, R = i-C_3H_7, 77589-34-5; V, R = t-C_4H_9, 77589-35-6; VI, R′ = OCH_3, R = CH_3, 77589-36-7; VI, R′ = OC_6H_5, R = CH_3, 77589-37-8; VI, R′ = n-BuNH, R = CH_3, 77589-38-9; VI, R′ = t-BuNH, R = CH_3, 77589-39-0; Cl_2, 7782-50-5; Br_2, 7726-95-6; I_2, 7553-56-2; $NaOCH_3$, 124-41-4; $NaOC_6H_5$, 139-02-6; n-$BuNH_2$, 109-73-9; t-$BuNH_2$, 75-64-9.

Supplementary Material Available: Haloalkylphosphazene infrared data (Table II) and NMR data (Table III) (8 pages). Ordering information is given on any current masthead page.

Contribution from Laboratoire CNRS-SNPE, 94320 Thiais, France,
and Laboratoire de Cristallochimie, Institut Le Bel, Université Louis Pasteur, 67070 Strasbourg Cedex, France

Bimetallic Sandwiches Based upon Phosphole Ligands

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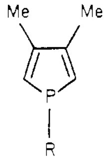
The reaction of a phosphole (L) with a σ,π complex $L'Fe_2(CO)_n$ (L′ = another phosphole; n = 6 or 7) gives the metallic sandwich $L[Fe_2(CO)_4]L'$. A heterobimetallic sandwich is also obtained when $L'FeMo(CO)_8$ is the starting compound. The X-ray crystal structure of the complex with L = L′ = 1-phenyl-3,4-dimethylphosphole has been determined. Crystal data: monoclinic, $C2/c$, with a = 14.334 (1) Å, b = 12.375 (1) Å, c = 16.470 (1) Å, β = 112.62 (1)°. The two phosphole rings adopt a head to tail disposition and are strongly folded. Very large ^{31}P–^{31}P NMR coupling suggests a direct through-space interaction between the nonbonded phosphorus and iron atoms.

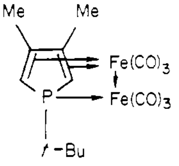
The fact that phospholes (L) can act as six-electron ligands by complexation of their phosphorus atoms and of their dienic systems with two different metal atoms was suspected as early as 1961[2] and was fully demonstrated more recently when the X-ray crystal structure of one $LMn_2(CO)_7$ complex[3] was established.[4] It has also been shown in our laboratory that the formation of a bond between the two complexed metals was dependent on the bulkiness of the phosphole P substituent.[5] Thus, when heated with triiron dodecacarbonyl, 1-phenyl-3,4-dimethylphosphole (**1**) gave an $LFe_2(CO)_7$ complex with no Fe–Fe bond whereas 1-*tert*-butyl-3,4-dimethylphosphole (**2**) gave a metal–metal bonded $LFe_2(CO)_6$ species. This intriguing observation was the starting point of a more exhaustive investigation of the reactions of iron carbonyls with phospholes, which led to the discovery of new types of bimetallic sandwiches described herein.

Results and Discussion

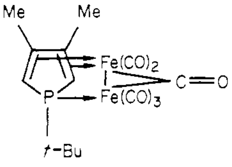
Synthesis. All our work has been carried out with phospholes **1** and **2**. At first we reinvestigated the reaction of **2** with $Fe_3(CO)_{12}$. In our previous work,[5] this reaction was performed at 110 °C in boiling toluene and gave predominantly the Fe–Fe bonded species **3**. Since no band could be ascribed to a bridging carbonyl in the IR spectrum of **3**, we proposed the structure **3A** for this complex. However, in view of the structural results of Weiss[6] on ferrole **4**, which had a semibridging carbonyl as shown despite the absence of $\nu(CO)$ absorptions in the bridging carbonyl region of the IR spectrum, the correct structure might be **3B**. Unfortunately the room-temperature ^{13}C NMR spectrum of **3** ($CDCl_3$, Me_4Si) did not allow us to choose between the two formulations since all the ^{13}CO resonances appeared equivalent on the NMR time scale [$\delta(CO)$ = 213.63; $J(C-P)$ = 5.8 Hz] contrary to what happens for ferrole **4**.[7] During this reinvestigation we also detected another complex to which we ascribed the structure **6** [identical with that of the main product (**5**) of the reaction of **1** with $Fe_3(CO)_{12}$] on the basis of the C, H, and Fe analysis, the IR spectrum (very similar to that of **5**), and the ^{31}P NMR spectrum [^{31}P δ(**6**) = 113.9, very close to the calculated value for **6**; see ref 5]. This complex was only a byproduct (maximum yield 10%) and disappeared completely if the reaction was run at 150 °C in boiling xylene. Thus it seemed that **6** decomposed to give **3** in boiling xylene, and we tried to extend this reaction to **5**. When heated at 150 °C in xylene for 24 h, **5** gave indeed a new complex but with the unexpected formula **7**. In view of this formula, which was fully established



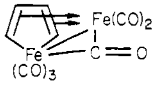
1, R = Ph
2, R = *t*-Bu



3A



3B



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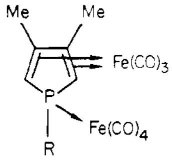
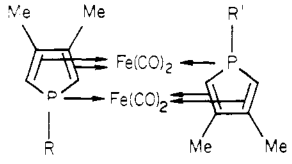


5, R = Ph
6, R = *t*-Bu



7, R = R′ = Ph
8, R = R′ = *t*-Bu
9, R = Ph, R′ = *t*-Bu

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(1) (a) Laboratoire CNRS-SNPE. (b) Institut Le Bel.

(2) E. H. Braye, W. Hubel, and I. Caplier, *J. Am. Chem. Soc.*, **83**, 4406 (1961).

(3) F. Mathey, *J. Organomet. Chem.*, **93**, 377 (1975).

(4) J. M. Rosalky, B. Metz, F. Mathey, and R. Weiss, *Inorg. Chem.*, **16**, 3307 (1977).

(5) F. Mathey and G. Muller, *J. Organomet. Chem.*, **136**, 241 (1977).

(6) G. Dettlaf and E. Weiss, *J. Organomet. Chem.*, **108**, 213 (1976).

(7) P. Hübener and E. Weiss, *J. Organomet. Chem.*, **129**, 105 (1977).

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