

Synthesis and Structure of Transition-Metal-Bound Phosphazenes Derived from Phosphazene Anions

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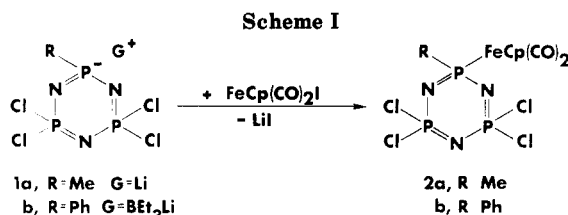
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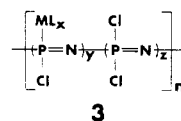
A synthetic procedure has been developed for the preparation of 1-phenyl-1-(carbonylcyclopentadienylmetallo)-3,3,5,5-tetrachlorocyclophosphazenes (7). These are prepared by the interaction of lithium (1-phenyl-3,3,5,5-tetrachlorocyclophosphazene-1-yl)triethylborate (1b) with $\text{MCp}(\text{CO})_n\text{I}$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$; $\text{M} = \text{Cr}, \text{Mo}, \text{W}, n = 3$; $\text{M} = \text{Fe}, \text{Ru}, n = 2$) in tetrahydrofuran in yields ranging from 15% to 100%. Species 1b is in equilibrium with lithium 1-phenyl-3,3,5,5-tetrachlorocyclophosphazene (5), a reactive species, with a phosphorus(III) center. The phosphorus(III) center in 5 reacts with $\text{CrCp}(\text{CO})_3\text{I}$, $\text{MoCp}(\text{CO})_3\text{I}$, $\text{WCp}(\text{CO})_3\text{I}$, and $\text{RuCp}(\text{CO})_2\text{I}$ by a carbonyl substitution pathway to give a thermally unstable anionic metallophosphazene, 6, in competition with the formation of 7. The structural features of 7 were examined by means of X-ray crystal and molecular structures of $\text{N}_3\text{P}_3\text{Cl}_4\text{PhMCp}(\text{CO})_n$ ($\text{M} = \text{Cr}$ (7a), Mo (7b), W (7c), $n = 3$; $\text{M} = \text{Fe}$ (7d), Ru (7e), $n = 2$). Crystals of 7a are monoclinic of space group $P2_1/n$ with $a = 14.911$ (1) Å, $b = 8.618$ (2) Å, $c = 16.544$ (3) Å, $\beta = 93.78$ (1)°, $V = 2121$ (1) Å³, and $Z = 4$. Crystals of 7b are triclinic of space group $P\bar{1}$ with $a = 8.447$ (3) Å, $b = 9.084$ (4) Å, $c = 14.682$ (2) Å, $\alpha = 75.54$ (2)°, $\beta = 76.15$ (2)°, $\gamma = 75.87$ (4)°, $V = 1038.8$ (7) Å³, and $Z = 2$. Crystals of 7c are triclinic of space group $P\bar{1}$ with $a = 8.425$ (3) Å, $b = 9.086$ (3) Å, $c = 14.628$ (5) Å, $\alpha = 75.40$ (3)°, $\beta = 76.05$ (3)°, $\gamma = 75.81$ (3)°, $V = 1031$ (2) Å³, and $Z = 2$. The structure of 7c was found to be analogous to that of 7b and thus was not fully solved. Crystals of 7d are monoclinic of space group $P2_1/n$ with $a = 8.113$ (1) Å, $b = 17.503$ (3) Å, $c = 14.215$ (2) Å, $\beta = 92.45$ (1)°, $V = 2016.6$ (9) Å³, and $Z = 4$. Crystals of 7e are monoclinic of space group $P2_1/n$, $a = 8.056$ (1) Å, $b = 17.624$ (4) Å, $c = 14.417$ (5) Å, $\beta = 91.63$ (2)°, $V = 2046$ (1) Å³, and $Z = 4$.

In recent years, we have developed a number of routes for the synthesis of organometallic cyclic and high polymeric phosphazenes.¹⁻¹² These approaches range from the use of pendent organic spacer groups to link transition metals to phosphazenes¹⁻⁴ to methods for the linkage of metals directly to the phosphorus atoms of the phosphazene skeleton.⁶⁻¹² These latter procedures involve the reactions of organometallic anions with halogenophosphazenes, processes that are often complicated by metal-halogen exchange side reactions. To avoid such side reactions, it is often necessary to employ *fluorophosphazenes* as reaction substrates rather than chlorophosphazenes. Unfortunately, fluorophosphazenes are more difficult to use as high polymers because of their restricted solubilities. Hence, the transfer of the small molecule organometallic substitution chemistry to high polymeric phosphazenes is difficult unless methods can be developed that involve the use of poly(dichlorophosphazene), $(\text{NPCl}_2)_n$.

In this present work, we have explored an alternative approach to the synthesis of cyclophosphazenes that bear phosphorus to transition-metal bonds. It involves the



preparation of phosphazene anions and their reactions with organometallic halides. A preliminary test of the feasibility of this approach was communicated earlier.⁵ In that work, we showed that phenyl- and methylcyclophosphazene anions 1 react with dicarbonylcyclopentadienyliron to give high yields of iron-bound cyclophosphazenes 2 (Scheme I). Here, we explore the scope of this reaction. In a later paper, we will describe the use of this chemistry at the high polymeric phosphazene level to yield macromolecular analogues such as 3.



Results and Discussion

The Overall Reaction. In this paper we report the reactions of a cyclophosphazene anion with carbonyl halides of group VIA (⁶²⁷) metals and ruthenium. It will be shown that, in general, this technique provides an excellent pathway to the preparation of a range of new organometallic cyclophosphazenes. As a model system, it also indicates the utility of the process for possible use in phosphazene high polymer chemistry. However, a competitive side reaction has been identified when $\text{CrCp}(\text{CO})_3\text{I}$, $\text{MoCp}(\text{CO})_3\text{I}$, $\text{WCp}(\text{CO})_3\text{I}$, or $\text{RuCp}(\text{CO})_2\text{I}$ react with chlorocyclophosphazenes. This reaction involves carbonyl displacement rather than halogen substitution.

The cyclophosphazene anion employed in this work was lithium (1-phenyl-3,3,5,5-tetrachlorocyclophosphazene-1-yl)triethylborate (1b), formed by the re-

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Table I. Infrared Data

compd	stretching freq, cm ⁻¹			
	CO ^a	CH ^b	PN ^b	PCI ^b
7a	2025 (s), 1954 (s, br)	3100, 3080, 3040	1185, 1172, 1158, 1148, 1113, 1096	578, 550, 512, 458
7b	2040 (s), 1960 (m, br), 1955 (s, br)	3100	1198, 1181, 1160, 1150, 1092	578, 545, 505, 480, 460
7c	2040 (s), 1955 (m, br), 1940 (s, br)	3095	1198, 1173, 1152, 1092	580, 535, 510, 490, 450
7d	2030 (s), 1980 (s), 1950 (m)	3100, 3055	1220, 1200, 1180, 1160, 1155, 1100	575, 555, 525, 505, 465, 435
7e	2042 (s), 1995 (s)	3100, 3050	1200, 1180, 1150, 1100	568, 551, 505, 460, 432
6a	1890 (s, br), ^c 1770 (s, br), 1720 (s, br)			

^aCO stretching frequencies were recorded as CH₂Cl₂ solutions in a NaCl cell. ^bCH, PN, and PCI stretching frequencies were recorded as KBr disks. ^cRecorded as a Nujol mull.

duction of bi(cyclophosphazene) 4 with lithium triethylborohydride in tetrahydrofuran.¹³ Species 1b reacts at room temperature or at reflux with organometallic halo complexes to give 1-(carbonylcyclopentadienylmetallo)-1-phenyl-3,3,5,5-tetrachlorocyclophosphazenes (7), as shown in Scheme II. The carbonyl displacement products are shown as species 6.

Reaction with FeCp(CO)₂I. Species 1b reacts with FeCp(CO)₂I (Cp = η⁵-C₅H₅) at 25 °C to give compound 7d in 90% yield.⁵ At 66 °C the yield rises to 100%. Thus, the reaction is characterized by a simple nucleophilic displacement of iodide by the phosphazene anion.

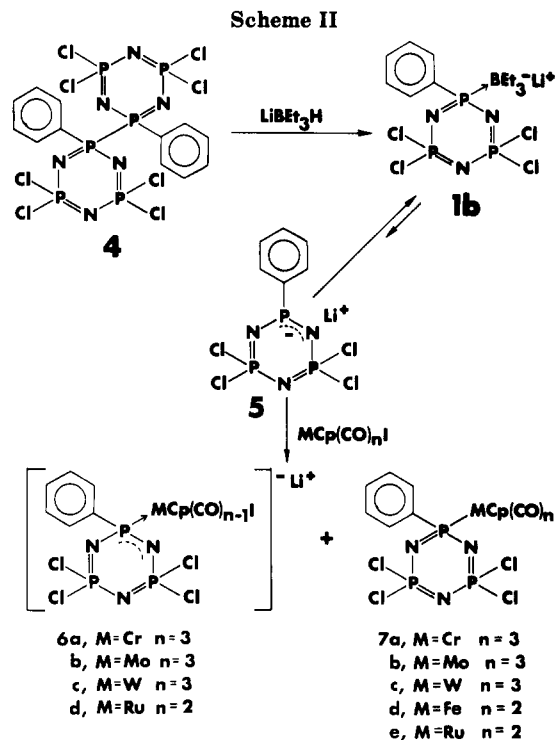
Reaction with CrCp(CO)₃I. By contrast, the reaction of 1b with CrCp(CO)₃I at 25 °C gives only a low yield of the expected product 7a together with a much larger yield of species 6a. The ratio of 7a to 6a was measured by ³¹P NMR spectroscopy to be 1:99. When the reaction of 1b with CrCp(CO)₃I was carried out under an atmosphere of carbon monoxide at high pressure, the ratio of 6a to 7a changed to 55:45. However, no conversion of 6a to 7a was detected when a 99:1 mixture of 6a and 7a was subjected to a high pressure of carbon monoxide. Thus, the formation of 6a and 7a is a competitive process, and 6a is not an intermediate in the formation of 7a.

The identity of 7a was established after the isolation of this compound from the reaction mixture (see later). However, species 6a could not be isolated as a pure compound, and its structure is based on indirect evidence, as discussed later.

Reactions with MoCp(CO)₃I, WCp(CO)₃I, and RuCp(CO)₂I. Anion 1b does not react with these three reagents in THF at 25 °C. However, at 66 °C, a 30%, 15%, and 20% conversion to 7b, 7c, and 7e occurs, respectively. No species corresponding to 6 were isolated, but evidence was obtained that 6b is formed as a short-lived product during the reaction of 1b with MoCp(CO)₃I.

For example, an examination of the ³¹P NMR spectra of the reaction mixture showed that the decline in concentration of 1b is accompanied initially by the appearance of peaks derived from 7b and larger quantities of 6b. At longer reaction times, species 6b decomposes and 7b is the only clearly identifiable product. In a separate experiment, 1b was allowed to interact with MoCp(CO)₃I at 66 °C under a high pressure of carbon monoxide. The yield of 7b increased to 70%. This evidence favors the view that a competition exists between iodide displacement and carbonyl displacement from the organometallic reagent.

Proof of Structure. The products of these reactions were characterized by a combination of ³¹P and ¹H NMR spectroscopy, infrared spectroscopy, mass spectrometry, and elemental microanalysis. These data are summarized in Tables I–III. The general technique is illustrated below for compounds 7b and 6a.



The structure of 7a was deduced as follows. The ³¹P NMR spectrum was interpreted as an AX₂ pattern that consisted of a triplet (P(Ph)(CrCp(CO)₃), 110.4 ppm) and a doublet (PCl₂, 8.9 ppm, J_{PNP} = 59.2 Hz). This is indicative of a cyclic phosphazene bearing unique substituents at one phosphorus. The large downfield shift of the A portion is consistent with a metal-substituted phosphazene, as is the large coupling constant. The ¹H NMR spectrum of 7a consisted of a doublet at δ 5.13 (J_{PMoCH} = 1.2 Hz) from the cyclopentadienyl protons and two unresolved multiplets at δ 7.87 and 7.45 from the phenyl ring protons. The infrared spectrum of 7a in CH₂Cl₂ showed carbonyl stretching absorptions at 2025 and 1954 cm⁻¹. The infrared spectrum contained aromatic CH stretching peaks at 3100 cm⁻¹ as well as the characteristic absorptions for a cyclic trimeric phosphazene ring (1185–1096 cm⁻¹) and P–Cl bonds (578–458 cm⁻¹). In the EI mass spectrum, the parent ion at m/z 553 was detected, together with a pattern corresponding to the successive loss of three carbonyl groups. In addition, the isotope pattern matched that calculated for the parent ion. The elemental microanalysis was consistent with the formula C₁₄H₁₀CrN₃O₃P₃. All these data are compatible with the proposed structure of 7a. Single-crystal X-ray structures were also obtained for 7a–e, and these will be discussed in detail in a later section.

In addition to the reaction chemistry described above, the following spectroscopic evidence supports the proposed structure of 6a. The ³¹P NMR spectrum of 6a was interpreted as an AX₂ pattern that consisted of a triplet

Table II. Mass Spectral and Elemental Analysis Data

compd	mass spectrum, <i>m/e</i>		elemental microanal.			
	EI	CI	calcd		found	
7a	553 (calcd 553)		C	30.30	C	30.06
			H	1.82	H	1.88
			N	7.57	N	7.25
7b	571 (calcd 599)	600 (M + 1)	C	28.10	C	28.28
			H	1.67	H	1.66
			N	7.02	N	7.00
7c	660 (calcd 688)	689 (M + 1)	C	24.48	C	24.75
			H	1.47	H	1.50
			N	6.12	N	6.13
7d	501 (calcd 529)	530 (M + 1)	C	29.37	C	29.22
			H	1.88	H	1.91
			N	7.91	N	7.76
7e	576 (calcd 576)		C	27.10	C	26.70
			H	1.75	H	1.71
			N	7.30	N	7.16

Table III. NMR Data^a

compd	³¹ P NMR, ppm		¹ H NMR, δ		coupling const, ^b Hz
	P(Ph)(M)	PCl ₂			
7a	110.4	8.9	C ₅ H ₅	5.13 (d)	<i>J</i> _{PNP} = 59.2
			C ₆ H ₅	7.87 (m)	<i>J</i> _{PCrCH} = 1.2
			C ₆ H ₅	7.45 (m)	
7b	89.2	8.8	C ₅ H ₅	5.55 (s)	<i>J</i> _{PNP} = 51.6
			C ₆ H ₅	7.82 (m)	<i>J</i> _{PMoCH} = 0.5
			C ₆ H ₅	7.43 (m)	
7c	52.3	9.0	C ₅ H ₅	5.68 (d)	<i>J</i> _{PNP} = 46.1
			C ₆ H ₅	7.78 (m)	<i>J</i> _{PWCH} = 0.8
			C ₆ H ₅	7.42 (m)	
7d	103.6	7.6	C ₅ H ₅	4.98 (d)	<i>J</i> _{PNP} = 42.0
			C ₆ H ₅	7.8 (m)	<i>J</i> _{PFcCH} = 1.2
			C ₆ H ₅	7.5 (m)	
7e	73.5	8.2	C ₅ H ₅	5.37 (s)	<i>J</i> _{PNP} = 32.3
			C ₆ H ₅	7.79 (m)	
			C ₆ H ₅	7.43 (m)	
6a	147.7	3.0			<i>J</i> _{PNP} = 84.5
6b	111.6	3.9			<i>J</i> _{PNP} = 71.1

^aAll data was recorded for solutions in CDCl₃. ^bUnlisted coupling constants were not resolved.

(P(Ph)(CrCp(CO)₂), 147.7 ppm) and a doublet (PCl₂, 3.0 ppm, *J*_{PNP} = 84.5 Hz). The downfield shift of the A portion is the largest yet detected for a monometallo-substituted phosphazene. The shift downfield relative to 7 is reminiscent of the coordinative behavior of similar phosphazene anionic species. In addition, the very large coupling constant is more typical of anionic phosphazenes than of neutral metallophosphazenes. An infrared spectrum of the reaction mixture, obtained after removal of the solvent, showed carbonyl absorbances at 1720, 1770, and 1890 cm⁻¹. This is suggestive of an anionic metal center.

Attempts were made to form crystalline derivatives of 6 by reactions with methyl iodide or bis(triphenylphosphine)nitrogen (1+) chloride, but crystals of the salts could not be obtained.

Reaction Mechanism. We assume that species 7b-e are formed by a nucleophilic attack by the phosphazene anion on the organometallic reagents, with displacement of iodide ion.

Species 6a and 6b appear to be formed by a competitive carbonyl displacement process. It is known that CrCp(CO)₃I reacts readily with phosphines and other phosphorus(III) ligands to give complexes of general formula CrCp(CO)₂(PR₃)I.¹⁸ This reaction may proceed through an initial dissociation of carbon monoxide, followed by coordination of the phosphine to the resultant coordinatively unsaturated chromium.

Anionic organophosphazenes are believed to be capable of equilibration between structures 1b and 5.¹³⁻¹⁷

Structure 5 contains a phosphorus(III) site that could coordinate to a coordinatively unsaturated chromium or molybdenum organometallic species. Thus, we propose that, by analogy with the well-known carbonyl displacement reaction, a molecule of carbon monoxide is displaced thermally from CrCp(CO)₃I or MoCp(CO)₃I and is replaced by the phosphorus(III) site of the phosphazene anion. In the chromium system, this appears to be the kinetically favored pathway. However, as discussed, under high pressures of excess carbon monoxide, the formation of 6a is retarded and the ratio of 7a to 6a changes from 1:99 to 1.2:1. This dramatic change reflects an influence on the dissociation of carbon monoxide from CrCp(CO)₃I. At the same time, more CrCp(CO)₃I is now available as a substrate for nucleophilic attack, and the yield of 7a rises accordingly. Species 6a is a distinct product formed in competition with 7a. It is not an intermediate, because exposure of a 1:99 ratio of 7a to 6a to high pressures of carbon monoxide did not shift the ratio to favor 7a.

X-ray Structural Determination. The X-ray crystallographic investigations of compounds 7a-e were carried

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Table IV. Crystallographic Data for Compounds 7a-e

	7a	7b	7c	7d	7e
crystal size	0.32 × 0.33 × 0.55	0.04 × 0.20 × 0.25	0.05 × 0.16 × 0.18	0.50 × 0.55 × 0.78	0.19 × 0.48 × 0.41
fw, amu	554.98	598.93	686.81	530.83	576.05
space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P2_1/n$
<i>a</i> , Å	14.911 (1)	8.447 (3)	8.425 (3)	8.113 (1)	8.056 (1)
<i>b</i> , Å	8.618 (2)	9.084 (4)	9.086 (3)	17.503 (3)	17.624 (4)
<i>c</i> , Å	16.544 (3)	14.682 (2)	14.628 (5)	14.215 (2)	14.417 (5)
α , deg		75.54 (2)	75.40 (3)		
β , deg	93.78 (1)	76.15 (2)	76.05 (3)	92.45 (1)	91.63 (2)
γ , deg		75.87 (4)	75.81 (3)		
<i>V</i> , Å ³	2121 (1)	1038.8 (7)	1031 (2)	2016.6 (9)	2046 (1)
<i>Z</i>	4	2	2	4	4
d_{calcd} , g cm ⁻³	1.738	1.915	2.212	1.748	1.870
2 θ max, deg	45.20	45.48		44.78	44.58
scan width, ($A + 0.347 \tan \theta$)°	0.75	1.00		1.00	0.80
total measd data	3142	2789		2916	2931
nonzero data	2678	2532		2497	2494
unique obsd data ($I > 2\sigma(I)$)	2537	2294		2374	2361
mean discrepancy for mult measd reflctns				0.046	0.020
μ , cm ⁻¹	12.80	13.85		15.31	15.24
anisotropic drift correct.	0.956-1.018	0.972-1.043		0.958-1.094	0.977-1.068
R_1/R_2	0.0321/0.0445	0.0364/0.0475		0.0334/0.0458	0.0282/0.0380
ρ (weighting factor)	0.030	0.055		0.020	0.020
esd	2.231	1.316		3.135	2.380
data/parameter	8.96	7.83		8.63	8.91
max shift/error	0.01	0.31		0.02	0.63
largest peak, ϵ Å ⁻³	0.42	0.78		0.30	0.40

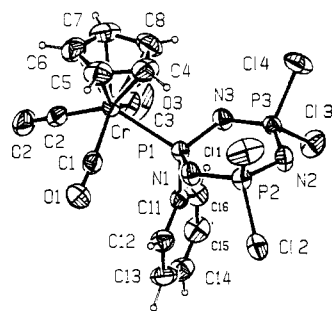


Figure 1. ORTEP diagram of compound 7a.

out both to confirm the molecular geometry and to investigate the effect of the various organometallic substituents on the structural parameters of the phosphazene ring.

A summary of cell constants and data collection parameters is included in Table IV. To permit comparisons between compounds 7a, 7b, 7d, and 7e, selected bond lengths and angles are included in Table V. Observed and calculated structure factor amplitudes are listed in Tables VI-IX. Atomic positional and thermal parameters are included in Tables X-XII. Bond lengths and angles are listed in Tables XIV-XVII and are included in Table V.

The solution of the X-ray crystal structures of compounds 7a, 7b, 7d, and 7e confirmed in each case that the molecules consisted of a tetrachlorochlorotriphosphazene ring with a phenyl ring and an $M\text{Cp}(\text{CO})_n$ unit attached to it geminally through P-C and P-M covalent bonds. The structure of 7c ($M = \text{W}$) was found to be similar to that of 7b, and a full structure solution was not obtained. All features of the structures were determined, including hydrogen atom positions. ORTEP views are given in Figures 1-3 for compounds 7a, 7b, 7d, and 7e, respectively.

The attachment of an organometallic substituent to a phosphazene ring greatly influences the structure of that ring. Evidence for this can be seen by comparison of the structural parameters for compounds 7a-e with those of a "control" structure that does not contain an organometallic side group. The monophenyl pentachloro-substituted phosphazene $\text{N}_3\text{P}_3\text{Cl}_5\text{Ph}$ ¹³ is a good model for

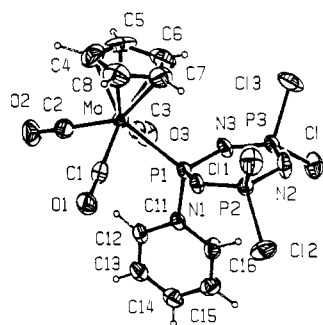
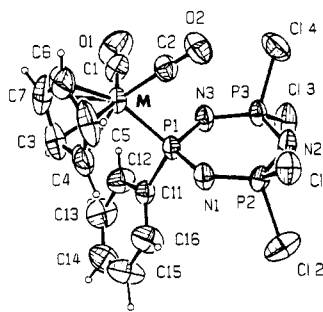


Figure 2. ORTEP diagram of compound 7b.

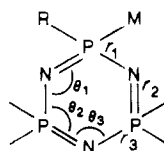


For Compound 7d $M = \text{Fe}$
For Compound 7e $M = \text{Ru}$

Figure 3. ORTEP diagram of compounds 7d and 7e.

comparison with the metallo-substituted phosphazenes prepared in this work. (See also Table V.)

The organometallic side group profoundly influences the structure of the ring in the immediate vicinity of the phosphorus atom P(1) to which it is linked. The following trends were found for each compound. A significant narrowing of the N-P-N angle occurs at the metal-substituted phosphorus atom compared with the situation in $\text{N}_3\text{P}_3\text{Cl}_5\text{Ph}$. The P-N bonds adjacent to P(1) are lengthened relative to the same bonds in $\text{N}_3\text{P}_3\text{Cl}_5\text{Ph}$. The effects of the metal on bond lengths are less evident at increasing distances from the P(1) atom. The remaining P-N bonds are similar in length to the corresponding bonds in

Table V. Selected Bond Angles and Distances for Compounds 7a-e and N₃P₃Cl₅Ph

	7a	7b	7d	7e	N ₃ P ₃ Cl ₅ Ph (M = Cl)
Angles (deg)					
M-P(1)-N(1)	110.73 (6)	110.5 (2)	110.8 (1)	112.47 (8)	106.5 (2)
M-P(1)-N(3)	109.78 (6)	109.1 (2)	111.4 (1)	111.50 (8)	107.4 (2)
M-P(1)-C(11)	114.96 (6)	117.2 (2)	112.2 (1)	110.27 (8)	103.5 (2)
N(1)-P(1)-N(3)	111.69 (8)	110.9 (2)	111.8 (1)	111.8 (1)	117.3 (2)
Cl-P-Cl (av)	99.71 (4)	98.7 (1)	99.21 (8)	99.22 (6)	101.4 (8)
θ ₁ (av)	121.7 (1)	123.8 (4)	123.6 (3)	123.4 (1)	121.6 (0)
θ ₂ (av)	120.7 (1)	120.3 (3)	120.4 (1)	120.5 (1)	119.0 (3)
θ ₃ (av)	118.2 (1)	118.6 (3)	118.5 (2)	118.4 (1)	120.9 (2)
P(1)-M-C(1)	76.54 (6)	73.7 (1)	89.0 (1)	87.32 (8)	
P(1)-M-C(2)	130.34 (6)	129.0 (2)	87.0 (1)	85.57 (8)	
P(1)-M-C(3)	77.37 (6)	74.8 (1)			
M-C-O (av)	176.8 (10)	177.7 (8)	178.1 (4)	178.4 (4)	
Distances (Å)					
M-P(1)	2.394 (1)	2.509 (1)	2.219 (1)	2.314 (1)	
P(1)-C(11)	1.819 (2)	1.824 (6)	1.806 (3)	1.812 (2)	1.778 (4)
r ₁ (av)	1.652 (3)	1.647 (6)	1.644 (4)	1.644 (3)	1.588 (2)
r ₂ (av)	1.549 (2)	1.550 (6)	1.545 (4)	1.543 (3)	1.556 (4)
r ₃ (av)	1.582 (3)	1.581 (6)	1.581 (4)	1.578 (3)	1.572 (5)
P-Cl (av)	2.005 (5)	2.009 (5)	2.007 (2)	2.004 (9)	1.987 (5)
M-Cp C (av)	2.191 (6)	2.322 (7)	2.086 (6)	2.235 (8)	
M-CO C (av)	1.866 (4)	1.997 (4)	1.765 (4)	1.833 (4)	
C-O	1.136 (1)	1.144 (4)	1.140 (6)	1.134 (4)	

N₃P₃Cl₅Ph, and the P-Cl bond lengths and Cl-P-Cl angles are normal. However, a considerable distortion exists in the phosphazene ring that becomes manifest in changes to the internal ring angles. In addition to the considerable narrowing of the N(1)-P(1)-N(3) angle, a widening occurs of the P(1)-N(1)-P(2) or P(1)-N(3)-P(3) angle, as well as a widening of the N-P-N angle at the phosphorus atoms that bear chlorine substituents. To compensate for this widening, the angle P(2)-N(2)-P(3) narrows considerably. The large change in the ring angles, accompanied by slight changes in bond lengths (except for P(1)-N), generates a considerable distortion from ring planarity.

Specifically, the angle N(1)-P(1)-N(3) narrows from 117.3 (2)° in N₃P₃Cl₅Ph to 110.9 (2)° in **7b**. The narrowing is slightly less pronounced in **7a** (111.69 (8)°) and in **7d** and **7e** (111.8 (1)° for both). This may be a consequence of a "scissoring" effect brought about by the widening of the exocyclic M-P-C angle at P(1) due to the steric bulk of the MCp(CO)_n and phenyl groups in combination with inductive effects from the metal. A further point of interest is the remarkable similarity of the N(1)-P(1)-N(3) angles in the different derivatives in spite of the large variations in exocyclic angles. The range of M-P(1)-C(11) angles for **7a-e** extends from 110.27 (8)° to 117.2 (2)°, yet N(1)-P(1)-N(3) varies only from 110.9 (2)° to 111.8 (1)°. An examination of these angles for every monometallo-substituted phosphazene prepared to date^{5,10} shows that N(1)-P(1)-N(3) varies from 112.3 (3)° in N₃P₃Cl₅CrCp(CO)₃ to 110.9 (2)° in **7b**. At the same time the exocyclic M-P-C angle varies from 108.5 (1)° in N₃P₃Cl₅CrCp(CO)₃ to 117.2 (2)° in **7b**. Clearly, changes in N(1)-P(1)-N(3) are limited by the geometry imposed by the ring or perhaps by intramolecular nonbonding covalent radii repulsions between N(1) and N(3).

The changes in PN bond lengths at increasing distances from the metal center follow the trend shown by all metallophosphazenes—i.e., a "long-short-medium" pattern. A comparison with the bond lengths in N₃P₃Cl₅Ph suggests that the P(1)-N lengths are altered the most when

a metallo substituent is present, possibly because the metal supplies electron density and thus lengthens the nearby P-N bonds. The remaining P-N bond lengths are quite similar to those found in N₃P₃Cl₅Ph.

However, when the remaining N-P-N and P-N-P angles of **7a-d** are compared with those of N₃P₃Cl₅Ph, it is apparent that the ring is distorted in response to the presence of an organometallic substituent at P(1). The greatest angular distortions are evident in the P-N-P angles. Specifically, θ₁ the average of P(1)-N(1)-P(2) and P(1)-N(3)-P(3) changes from 121.6 (0)° in N₃P₃Cl₅Ph to 123.8 (4)° in **7b**. Compound **7a** is anomalous in that θ₁ remains at 121.7 (1)°. Angle θ₂, the average of the N(1)-P(2)-N(2) and N(3)-P(3)-N(3) angles, changes from 119.0 (3)° in N₃P₃Cl₅Ph to 120.7 (1)° in **7a**. Angle θ₃, the P-N(2)-P angle, averages 118.4 (3)° for **7a-e**. This can be compared to 120.9 (2)° in N₃P₃Cl₅Ph. Clearly, much of the distortion appears at the ring nitrogen atom most distant from the metallo-substituted phosphorus.

The metal-phosphorus bond distances for compounds **7a-e** are comparable to those observed in other metallo-phosphazenes. In addition, the structural parameters of the cyclopentadienyl rings and carbonyl ligands are normal.

Experimental Section

Materials and Equipment. Tetrahydrofuran (THF) and hexane were distilled from sodium benzophenone ketyl under nitrogen before use. LiBEt₃H (Aldrich) was used as received. CrCp(CO)₃I,¹⁸ MoCp(CO)₃I,¹⁸ RuCp(CO)₂I,¹⁹ and WCp(CO)₃I²¹ were prepared according to modified literature procedures. Species (N₃P₃Cl₄Ph)₂ was prepared according to a previously published procedure.²⁰ ³¹P NMR spectra were recorded with the

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use of either a Varian CFT-20 instrument operating at 32 MHz or a Bruker WP-200 unit operating at 80 MHz, both in the Fourier transform mode. Positive chemical shifts are downfield from external 85% phosphoric acid. ^1H NMR spectra were recorded on a Bruker WP-200 instrument operating at 200 MHz in the Fourier transform mode. Positive chemical shifts are downfield from Me_4Si . Infrared spectra were recorded on a Perkin-Elmer 283B spectrometer. Carbonyl region spectra were recorded for dichloromethane solutions in a sodium chloride solution cell. Full range spectra were recorded as potassium bromide disks. Electron-impact mass spectra were obtained with the use of a KRATOS MS9/50 spectrometer. Chemical ionization mass spectra were recorded on a Finnegan 3200 GC/MS system using methane as a reagent gas. Elemental microanalysis was obtained by Galbraith Laboratories, Knoxville, TN. All reactions were carried out under an atmosphere of dry nitrogen by using standard Schlenk techniques unless otherwise indicated.

Preparation of Anion 1b. Species $(\text{N}_3\text{P}_3\text{Cl}_4\text{Ph})_2$ (2.0 g) was dissolved in dry THF (30 mL). LiBEt_3H (2.5 equiv) (7.1 mL of a 1.0 M in THF solution) was added via syringe, and the mixture was stirred for 2 h. ^{31}P NMR spectroscopy confirmed the formation of 1b.¹³

General Procedure for the Interaction of 1b and Organometallic Reagents. As a representative procedure, 1.0 equiv of the organometallic reagent was dissolved in THF (15 mL) and transferred to the solution of the anion by means of a double-tipped syringe. The reaction mixture was stirred at room temperature for 24 h, and a ^{31}P NMR spectrum was then recorded. The criterion for the effectiveness of the reaction was the disappearance of the $\text{P}(\text{Ph})(\text{BEt}_3\text{-Li}^+)$ and PCl_2 resonances of the anion. If no reaction had occurred by this time, the reaction mixture was heated to reflux for 24 h and another ^{31}P NMR spectrum was recorded. Tetrahydrofuran was removed in vacuo, and the reaction mixture was then chromatographed on coarse silica gel with dichloromethane/hexanes mixtures. Some decomposition occurred during chromatography. Recrystallization from dichloromethane/hexanes gave analytically pure samples of the metallophosphazenes as yellow, air-stable, crystalline solids which decomposed in solution when exposed to air.

The Reaction of 1b with $\text{CrCp}(\text{CO})_3\text{I}$. Compound 1b was prepared as described above. Species $\text{CrCp}(\text{CO})_3\text{I}$ (1.86 g, 5.65 mmol) was dissolved in dry THF (15 mL) and was transferred to the solution of the anion via a double-tipped syringe. After 24 h at room temperature, the ^{31}P NMR spectrum showed a complete disappearance of the anion and appearance of a new AB_2 pattern (A (t) 147.8 ppm; B₂ (d) 3.1 ppm; $J_{\text{PNP}} = 84.1$ Hz) and a very small component of the AB_2 pattern corresponding to 7a in approximate proportions of 99:1. During chromatography the reaction mixture adsorbed strongly to the column support and changed color from yellow to green. Only a small amount of 7a was recovered (0.006 g).

The Reaction of 1b with $\text{CrCp}(\text{CO})_3\text{I}$ under CO Pressure. Compound 1b was prepared as described above. A stainless-steel pressure reactor was charged with the solution of the anion, a tube containing $\text{CrCp}(\text{CO})_3\text{I}$ (1.86 g, 5.65 mmol) and carbon monoxide (65 atm). After being sealed, the reactor was agitated to mix the contents. The contents were then stirred for 24 h. A ^{31}P NMR spectrum of the mixture showed the presence of 7a and 6a in proportions of 45:55. Column chromatography on coarse silica gel with dichloromethane/hexanes afforded 7a (0.5 g) as a yellow solid (16% yield). An analytical sample was prepared by recrystallization from dichloromethane/hexanes. The reaction of 1b with $\text{CrCp}(\text{CO})_3\text{I}$ was repeated at atmospheric pressure, and the reaction mixture was then placed in a pressure reactor after the ^{31}P NMR spectrum showed that all of 1b had disappeared. The reactor was then charged with 65 atm of carbon monoxide and stirred for 24 h. A ^{31}P NMR spectrum recorded at this time showed that no additional 7a had been formed.

Reaction of 1b with $\text{MoCp}(\text{CO})_3\text{I}$, $\text{WCp}(\text{CO})_3\text{I}$, and $\text{RuCp}(\text{CO})_2\text{I}$. These reactions were carried out in the manner described above. After 24 h at 66 °C, ^{31}P NMR spectra of the reaction mixture showed only 7 and a broad set of resonances centered at 18 ppm. Separation by chromatography afforded 7b, 7c, and 7e in 15%, 8%, and 10% yields, based on the starting material 4. The decomposition products obtained by heating the 99:1 mixture of 6a/7a to 66 °C for 24 h gave the same ^{31}P NMR

spectrum as those generated by the decomposition of 6. Again, only 7a and peaks assigned to decomposition products of 6a were detected. ^{31}P NMR monitoring of the reaction of 1b with $\text{MoCp}(\text{CO})_3\text{I}$ at intervals of 1 h showed that, as 1b disappeared, 6b and 7b formed, but 6b decomposed shortly after it was formed. Reaction of 1b with $\text{MoCp}(\text{CO})_3\text{I}$ under high pressures of carbon monoxide, following the procedure outlined above for $\text{CrCp}(\text{CO})_3\text{I}$, improved the conversion to 7b from 30% to approximately 75%.

X-ray Crystal Structure Determination Technique. The structural determination of 7a will be described as an illustration of the methods used. Crystals of $\text{N}_3\text{P}_3\text{Cl}_4\text{PhCrCp}(\text{CO})_3$ were grown from dichloromethane layered with hexanes at -4 °C. A transparent yellow crystal, 0.32 mm × 0.33 mm × 0.5 mm, was mounted on a glass fiber, which was then transferred to a eucentric goniometer head and attached to an Enraf-Nonius CAD4 automated diffractometer controlled by a PDP11 computer. A full rotation orientation photograph was taken with a Polaroid cassette accessory, and 25 reflections of moderate intensity were chosen and centered with the use of the Enraf-Nonius programs.²³ These reflections were used to obtain an orientation matrix for data collection. They suggested a monoclinic cell of dimensions $a = 14.911$ (1) Å, $b = 8.618$ (2) Å, and $\beta = 93.78$ (1)° with $V = 2121$ (1) Å³. The observed volume is consistent with that expected for $Z = 4$ and $d(\text{calcd}) = 1.738$ g cm⁻³. The observed systematic absences ($0k0$, $k = 2n + 1$; $h0l$, $h + l = 2n + 1$) suggested the space group $P2_1/n$ (nonstandard setting $P2_1/c$, no. 14).²⁴

A graphite single-crystal incident-beam monochromator was used for data collection with Mo $K\alpha$ radiation (λ (Mo $K\alpha_1$) = 0.71073 Å) at room temperature (21 °C) (takeoff angle = 2.80°). A θ - 2θ scan method was used with a variable scan rate ranging from 5°/min for the most intense reflections to 1°/min for the weaker ones. The angular scan width (ω) was variable and amounted to $(0.75 + 0.347 \tan \theta)$ ° both below $K\alpha_1$ and above $K\alpha_2$. Right and left backgrounds were each scanned for 25% of the total scan time. During data collection, three "standard" reflections were recorded after every 60 min of actual X-ray exposure time and were recentered after every 350 reflections to monitor crystal stability and orientation. The standard reflections were used to rescale data automatically to correct for drift during data collection (anisotropic drift corrections were random and varied from 0.956 to 1.018). A total of 3142 reflections were collected for $3.2 \leq 2\theta \leq 45.20$; multiply measured reflections were averaged (discrepancy 0.020) giving 2678 unique nonzero reflections; of these 2537 had intensities with $I \geq 2\sigma(I)$ and were considered observed. No correction was made for absorption ($\mu = 12.80$ cm⁻¹ for Mo $K\alpha$).

The heavy atoms were located from a sharpened, origin-removed Patterson map and were confirmed by a direct methods solution. Additional non-hydrogen atoms were located with successive Fourier syntheses. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located and were refined with fixed isotropic thermal parameters, $B = 5.0$ Å². Neutral atom scattering factors were used for all atoms²⁵ and were corrected for anomalous dispersion²⁴ by using both real and imaginary parts. Refinement of all anisotropic thermal parameters of all non-hydrogen atoms and both hydrogen and non-hydrogen positional parameters using a non-Poisson distribution type weighting scheme (weighting factor = 0.30) yielded $R_2 = 0.0445$.²⁶ In the final cycle the maximum shift was 0.01 esd. Final difference Fourier maps showed the largest peak to be 0.42 e Å⁻³.

(23) All programs used in data collection, reduction, and refinement were part of the Enraf-Nonius Structure Determination Package (SDP), Enraf-Nonius, Delft, Holland, 1975, revised 1977.

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(26) $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $R_2 = \{ \sum \omega (|F_o| - |F_c|)^2 \}^{1/2}$.

(27) In this paper the periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

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Registry No. 1b, 86727-36-8; 4, 21229-71-0; 6a, 104323-06-0; 7a, 104323-02-6; 7b, 104323-03-7; 7c, 104323-04-8; 7d, 88043-06-5; 7e, 104323-05-9; FeCp(CO)₂I, 12078-28-3; CrCp(CO)₃I, 32628-88-9;

MoCp(CO)₃I, 12287-61-5; WCp(CO)₃I, 31870-69-6; RuCp(CO)₂I, 31781-83-6.

Supplementary Material Available: Tables of atomic positional and thermal parameters and bond distances and angles for 7a, 7b, 7d, and 7e (18 pages); listings of structure factor amplitudes for 7a, 7b, 7d, and 7e (49 pages). Ordering information is given on any current masthead page.

Tellurapyrylium Dyes. 3. Oxidative Halogen Addition and Tellurium-Halogen Exchange

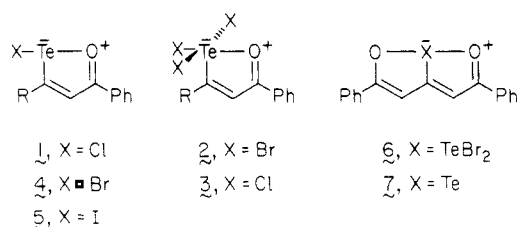
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The oxidative addition of halogens to tellurapyrylium dyes gives 10-Te-4 telluranes. The absorption maxima of the oxidative addition products are shifted hypsochromically relative to the parent tellurapyrylium salt. The structure of the oxidative addition products was determined unambiguously for one dye by single-crystal X-ray crystallography. Fluxional behavior was observed in the ¹H NMR spectra of one of the products as a result of tellurium-halogen exchange. The exchange was first-order with respect to the dye in CD₃CN and second-order in CDCl₂CDCl₂. In CDCl₃, the exchange was a mixture of first- and second-order processes. The line shapes from variable-temperature ¹H NMR were matched to line shapes generated by computer simulation with the program DNMR3 to give the kinetics of the exchange. The oxidative addition products are easily reduced, as shown by cyclic voltammetry.

Organotellurium compounds easily exchange halogen ligands with other halogens or with other organotellurium compounds in which the Te atoms are in a lower oxidation state. For example, the addition of 1 equiv of bromine to oxatellurolylium chlorides 1 gives a 2:1 mixture of pertellurane trihalides 2 and 3, respectively.¹ Similarly, the addition of chlorine to oxatellurolylium bromides 4 gives a 1:2 mixture of 2 and 3, respectively.¹ The addition of bromine to oxatellurolylium iodides 5 gives pertellurane tribromides 2 plus iodine. The dioxatellurapentalene dibromide 6 reacts with diphenyltelluride to give dioxatellurapentalene 7 and diphenyltellurium dibromide.² These exchanges are rapid and are completely driven to products.



In a series of studies, Nefedov et al. used isotopic labeling to follow halogen exchange between diphenyltellurium dihalides and diphenyltelluride.³ The exchange reactions involving diphenyltellurium dichloride, dibromide, and diiodide were second-order reactions, first-order with respect to both dihalide and diphenyl telluride. A change in mechanism was observed for the halogen exchange between diphenyltellurium difluoride and diphenyl

telluride. This exchange was a first-order reaction with respect to the difluoride.^{3a}

We wish to report the synthesis, structure, and properties of a new class of 10-Te-4 telluranes formed by the oxidative addition of a halogen molecule across a Te atom of a tellurapyrylium dye. Some of the resulting dyes display fluxional behavior, as shown by ¹H NMR, resulting from Te-halogen exchange. The kinetics and activation parameters for the exchange for one dye were determined by variable-temperature ¹H NMR and computer-simulated line-shape matching using the program DNMR3.⁴

Results and Discussion

Preparation and Structure. The addition of bromine to a solution of tellurapyrylium dye 8 in CH₂Cl₂ gave a red solution. The black solid isolated from this solution gave shiny, black needles of 9 upon recrystallization from CH₃CN. The structure of 9 was determined unambiguously by single-crystal X-ray crystallography.

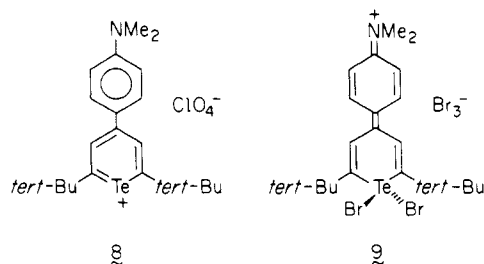


Figure 1 shows a plot of the molecule with atomic labeling. For clarity, only the A positions for the disordered methyls are shown. The thermal ellipsoids were plotted at the 40% probability level. Tables of bond distances and angles, least-squares planes, and positional and thermal parameters are given in the supplementary material.

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