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Transition-Metal Derivatives of Phosphinophosphazenes: X-ray Crystal Structures of $N_3P_3Cl_4PhPPh_2$, $N_3P_3Cl_4PhPPh_2 \cdot Cr(CO)_5$, and $N_3P_3Cl_4PhPPh_2 \cdot Ru_3(CO)_{11}$

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The phosphinophosphazene $N_3P_3Cl_4PhPPh_2$ (**1**) has been synthesized by the reaction of the triethylborane-stabilized phosphazene anion in $Li[N_3P_3Cl_4PhBEt_3]$ (**4**) with PPh_2Cl. The arsinophosphazene $N_3P_3Cl_4PhAsPh_2$ (**12**), the first example of a phosphazene with a P–As bond, was similarly synthesized from **4** and $AsPh_2Cl$. The phosphino group of **1** undergoes facile coordination to low-valent transition-metal fragments; coordination to skeletal nitrogen atoms of the phosphazene ring was not detected. Reaction of **1** with (i) $Cr(CO)_6$ (under ultraviolet irradiation) or $Cr(CO)_5THF$ or with (ii) $Fe_2(CO)_9$ affords the mononuclear complexes $N_3P_3Cl_4PhPPh_2 \cdot Cr(CO)_5$ (**5**), and $N_3P_3Cl_4PhPPh_2 \cdot Fe(CO)_4$ (**6**), respectively. Heating of **1** with $Ru_3(CO)_{12}$ gives the polynuclear species $N_3P_3Cl_4PhPPh_2 \cdot Ru_3(CO)_{11}$ (**7**). The structures of **1**, **5**, and **7** have been determined by X-ray diffraction. Crystals of **1** are monoclinic, space group $P2_1/c$, with $a = 18.007$ (7) Å, $b = 8.447$ (3) Å, $c = 16.999$ (6) Å, $\beta = 116.95$ (3)°, $V = 2304.8$ Å^3, and $Z = 4$. Crystals of **5** are monoclinic, space group $P2_1/c$, with $a = 17.245$ (9) Å, $b = 17.901$ (2) Å, $c = 9.990$ (7) Å, $\beta = 93.95$ (6)°, $V = 3076.6$ Å^3, and $Z = 4$. Crystals of **7** are monoclinic, space group $P2_1$, with $a = 9.498$ (6) Å, $b = 35.275$ (12) Å, $c = 13.457$ (4) Å, $\beta = 108.05$ (3)°, $V = 4286.7$ Å^3, and $Z = 4$. The P–P bonds of **1**, **5**, **6**, and **7** and the P–As bond of **12** are sources of hydrolytic instability and were shown (in the cases of **1**, **6**, and **12**) to undergo nucleophilic cleavage with sodium trifluoroethoxide. High polymeric phosphazenes bearing backbone-bound phosphino groups have been synthesized in solution but are also hydrolytically sensitive and decompose on attempted isolation.

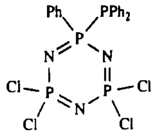
Introduction

The synthesis of macromolecules that function as carrier species for transition metals is of considerable interest because of their potential application as electroactive materials and polymer-supported catalysts.

In recent years, we have described the synthesis of polyphosphazenes in which metals are bound to skeletal phosphorus atoms by covalent bonds,[1] via coordination to skeletal nitrogen atoms,[2,3] or by the use of pendent organic spacer groups.[4-9] A prudent prerequisite for the synthesis of such high polymeric species is the initial examination of prototype systems at the small molecule level. This protocol is usually followed because of the greater ease of characterization of small molecules compared to macromolecules.[10]

Phosphino groups linked via spacer units have been used previously to bind transition metals to polyphosphazenes.[6,7] However, we are particularly interested in the synthesis of macromolecules in which transition metals are held in close proximity to the polymer backbone. In certain cases, this may facilitate bonding interactions between adjacent metal sites, leading to the possibility of one-dimensional electronic conduction.[11] In this paper, we describe the attachment of transition metals to a cyclophosphazene in which a phosphino group is directly bound to the phosphorus–nitrogen skeleton by a P–P bond. Specifically, the phosphinophosphazene **1** was synthesized and its coordination chemistry studied. During these studies **1** was viewed as a model for prospective high polymeric phosphazene analogues such as **2**.

In the course of these investigations, we hoped to answer the following questions: (a) Would transition metals bind exclusively to the phosphino group or would coordination to skeletal nitrogen atoms also take place? (b) What structural influence would a phosphino substituent have on the cyclophosphazene ring? (c) How might this structural effect be modified following coordination to the phosphino group? (d) How would the stability of the P(V)–P(III) bond compare to that of the hydrolytically stable P(V)–P(V) bond of bi(cyclophosphazenes) on one hand and the more labile P(III)–P(III) bond of diphosphines on the other? This question has an important bearing on the possible extension of the work to the macromolecular level.



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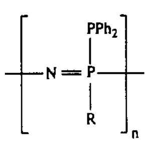

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Results and Discussion

Synthesis and Characterization of the Phosphinophosphazene 1. The phosphinophosphazene **1** was synthesized in high yield by the reaction of the chlorophosphine PPh_2Cl with the triethylborane-stabilized phosphazene anion **4**[12] (prepared by cleavage of the bi(cyclophosphazene) **3** with $Li[BEt_3H]$) (Scheme I). The structure of **1** was established by ^{31}P NMR, elemental analysis, and mass spectrometry. Thus, the proton-decoupled ^{31}P NMR spectrum of **1** shows a relatively high-field doublet of triplets at −14.0 ppm ($^1J_{PP} = 237$ Hz, $^3J_{PPNP} = 9$ Hz) assigned to the phosphorus atom of the diphenylphosphino group, a lower field doublet of triplets at 37.9 ppm ($^1J_{PP} = 237$ Hz, $^2J_{PNP} = 18$ Hz) assigned to the phosphorus atom bearing the phosphino substituent, and a doublet of doublets at 16.3 ppm ($^2J_{PNP} = 18$ Hz, $^3J_{PPNP} = 9$ Hz) assigned to the PCl_2 units. The electron-impact mass spectrum of **1** showed the expected molecular ion (m/z 539) and isotope pattern.

The only other reported phosphinophosphazenes were synthesized by Schmidpeter and co-workers[13] who prepared the compounds $N_3P_3Ph_4MePR^1R^2$ (R^1 or R^2 = Me, Ph, or OCH_2CH_2O) by reaction of the hydridophosphazene $N_3P_3Ph_4MeH$ with PR^1R^2Cl followed by deprotonation of the resulting cationic product with anhydrous NH_3. No X-ray crystallographic data on these compounds existed. Thus, an X-ray structure determination of **1** was undertaken.

X-ray Structure Determination of 1. The molecular structure of **1** is shown in Figure 1. A summary of cell constants and data collection parameters is included in Table I. Final fractional atomic coordinates and selected bond lengths and angles are given in Tables II and III, respectively.

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Scheme I

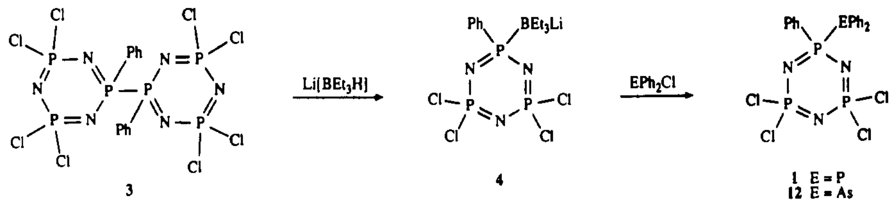

Table I. Summary of Crystal Data and Intensity Collection Parameters

	1	5	7
formula	$C_{18}H_{15}N_3P_4Cl_4$	$C_{23}H_{15}Cl_4N_3P_4O_5Cr$	$C_{29}H_{15}Cl_4N_3O_{11}P_4Ru_3\cdot 0.5C_7H_8$
fw	539.05	731.10	1196.44
cryst size, mm	0.36 × 0.34 × 0.08	0.54 × 0.20 × 0.10	0.45 × 0.45 × 0.22
space group	$P2_1/c$	$P2_1/c$	$P2_1$
a, Å	18.007 (7)	17.245 (9)	9.498 (6)
b, Å	8.447 (3)	17.901 (2)	35.275 (12)
c, Å	16.999 (6)	9.990 (7)	13.457 (4)
β, deg	116.95 (3)	93.95 (6)	108.05 (3)
V, Å^3	2304.8	3076.6	4286.7
Z	4	4	4
D(calcd), g/cm^3	1.553	1.578	1.853
radiation	Mo Kα	Mo Kα	Mo Kα
θ limits, deg	23	23	25
μ, cm^{-1}	8.013	9.554	14.83
λ, Å	0.71073	0.71073	0.71073
T, K	293	293	293
scan method	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
ω–scan width ($A + 0.35 \tan\theta$), deg	0.70	0.80	1.00
cryst decay, %	11.8	1.6	none
empirical abs cor			
min cor factor	0.9155	0.7135	0.9217
max cor factor	0.9991	0.9995	0.9999
no. of unique data measured	3460	4582	7662
no. of data used [$I > 3\sigma(I)$]	1798	3225	5765
data:param ratio	6.9	8.9	9.6
R, R_w ($=\Sigma\Delta^2/\Sigma wF_o^2)^{1/2}$)	0.039, 0.046	0.071, 0.091	0.060, 0.086
(Δ/σ)max in last cycle	0.01	0.01	<0.1
$\Delta\rho$ in final ΔF map, e Å^{-3}	0.30	1.05	0.76
final ρ param in wtg scheme	0.060	0.05	0.070

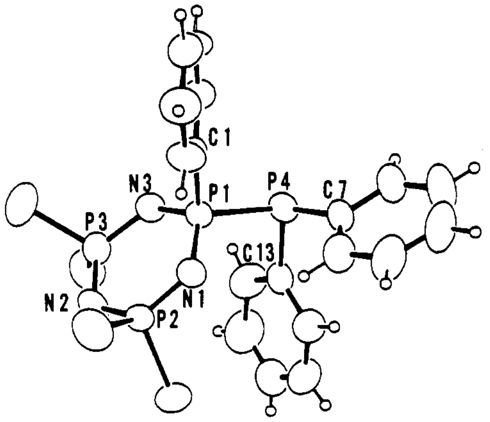

Figure 1. Molecular structure of **1**.

Table II. Final Fractional Atomic Coordinates for Non-Hydrogen Atoms of **1**

atom	x	y	z
Cl(1)	0.5448 (1)	0.7258 (3)	0.7601 (1)
Cl(2)	0.5386 (1)	0.9741 (2)	0.6257 (1)
Cl(3)	0.6246 (1)	0.6167 (2)	0.4731 (1)
Cl(4)	0.6231 (1)	0.3319 (2)	0.5852 (1)
F(1)	0.7677 (1)	0.7313 (2)	0.7350 (1)
P(2)	0.5997 (1)	0.7770 (2)	0.6854 (1)
P(3)	0.6458 (1)	0.5640 (2)	0.5961 (1)
P(4)	0.8578 (1)	0.6103 (2)	0.8549 (1)
N(1)	0.6925 (2)	0.8178 (5)	0.7444 (2)
N(2)	0.5763 (2)	0.6461 (6)	0.6133 (3)
N(3)	0.7387 (2)	0.5930 (5)	0.6611 (2)
C(1)	0.8249 (3)	0.8792 (6)	0.7090 (3)
C(2)	0.8018 (3)	1.0369 (6)	0.7003 (3)
C(3)	0.8445 (3)	1.1472 (7)	0.6767 (4)
C(4)	0.9106 (3)	1.1018 (7)	0.6645 (3)
C(5)	0.9349 (3)	0.9487 (7)	0.6729 (3)
C(6)	0.8924 (3)	0.8350 (7)	0.6950 (3)
C(7)	0.8911 (3)	0.7625 (7)	0.9397 (3)
C(8)	0.9731 (3)	0.7519 (7)	1.0027 (3)
C(9)	1.0040 (4)	0.8538 (8)	1.0741 (4)
C(10)	0.9536 (4)	0.9660 (8)	1.0826 (4)
C(11)	0.8735 (4)	0.9811 (8)	1.0195 (4)
C(12)	0.8416 (3)	0.8798 (7)	0.9487 (3)
C(13)	0.7827 (3)	0.4910 (6)	0.8744 (3)
C(14)	0.7535 (3)	0.5309 (7)	0.9334 (3)
C(15)	0.6980 (3)	0.4303 (8)	0.9447 (3)
C(16)	0.6728 (3)	0.2947 (8)	0.8982 (4)
C(17)	0.7013 (4)	0.2538 (7)	0.8409 (4)
C(18)	0.7575 (3)	0.3509 (7)	0.8290 (3)

The X-ray crystal structure of **1** confirmed the presence of a tetrachlorocyclotriphosphazene ring with a phenyl substituent and a diphenylphosphino unit attached to it geminally through P–C and P–P covalent bonds, respectively. The presence of a diphenylphosphino substituent significantly influences the structure of the phosphazene ring. Evidence for this may be seen by comparison of the structural parameters for **1** with those of $N_3P_3Cl_5Ph$,[12] which does not possess a phosphino side group (see Table II). Specifically, a significant widening of the exocyclic C(1)–P(1)–P(4) bond angle at the phosphino-substituted phosphorus atom occurs (ca 3.2°) compared to the situation in $N_3P_3Cl_5Ph$. This is accompanied by a narrowing of the N(1)–P(1)–N(3) angle of ca 2.8°. The P–N bonds adjacent to P(1) are lengthened by an average of 0.03 Å relative to the same bonds in $N_3P_3Cl_5Ph$. The effect of the phosphino substituent on the P–N bond lengths and N–P–N bond angles decreases at increasing distances from the P(1) atom, and the remaining P–N bonds are

Table III. Selected Bond Lengths and Angles for Compounds **1**, **5**, **7a**, **7b**, and $N_3P_3Cl_5Ph$

	bond lengths, Å				
	1	**5**	**7a**	**7b**	$N_3P_3Cl_5Ph$[a]
P(1)-N(1)	1.611 (5)	1.607 (5)	1.63 (2)	1.63 (1)	1.590 (4)
P(1)-N(3)	1.619 (5)	1.602 (5)	1.57 (1)	1.62 (2)	1.587 (4)
P(2)-N(1)	1.548 (3)	1.559 (6)	1.57 (1)	1.57 (2)	1.554 (3)
P(3)-N(3)	1.551 (3)	1.553 (6)	1.59 (2)	1.53 (2)	1.559 (4)
P(2)-N(2)	1.561 (5)	1.580 (6)	1.57 (2)	1.54 (2)	1.575 (4)
P(3)-N(2)	1.570 (6)	1.587 (7)	1.57 (2)	1.56 (2)	1.568 (4)
P-Cl (av)	1.992 (2)	1.993 (3)	1.99 (1)	2.00 (1)	2.005 (5)
P(1)-P(4)	2.199 (2)	2.234 (2)	2.24 (1)	2.26 (1)	
P(1)-C(1)	1.798 (5)	1.789 (7)	1.80 (3)	1.80 (2)	1.778 (4)
P(4)-C(7)	1.819 (5)	1.829 (6)	1.83 (2)	1.88 (2)	
P(4)-C(13)	1.834 (6)	1.830 (6)	1.83 (2)	1.84 (2)	
P(4)-M		2.387 (2)	2.345 (4)	2.341 (4)	
$M-CO_{cis}$ (av)		1.891 (7)			
$M-CO_{trans}$		1.855 (7)			

	angles, deg				
	1	**5**	**7a**	**7b**	$N_3P_3Cl_5Ph$[a]
N(1)-P(1)-N(3)	114.5 (2)	114.8 (3)	116.7 (9)	115.1 (8)	117.3 (2)
P(1)-N(3)-P(3)	122.1 (3)	123.4 (3)	122.0 (1)	122.5 (8)	121.6 (2)
P(1)-N(1)-P(2)	123.0 (3)	122.5 (3)	120.6 (7)	120.0 (1)	121.6 (2)
N(2)-P(3)-N(3)	119.4 (2)	119.1 (4)	119.0 (8)	120.0 (1)	119.2 (2)
N(1)-P(2)-N(2)	119.7 (2)	119.3 (3)	120.0 (1)	118.7 (8)	118.8 (2)
P(2)-N(2)-P(3)	120.3 (2)	119.9 (5)	120.0 (1)	122.0 (1)	120.9 (2)
Cl-P-Cl (av)	100.8 (1)	100.1 (2)	101.0 (4)	100.0 (3)	101.4 (5)
C(1)-P(1)-P(4)	106.7 (1)	107.0 (2)	102.3 (7)	104.3 (7)	103.5 (2)
N(3)-P(1)-P(4)	103.1 (1)	107.2 (3)	109.2 (7)	108.5 (6)	
N(1)-P(1)-P(4)	114.8 (2)	108.6 (3)	106.6 (6)	111.2 (6)	
P(1)-P(4)-C(7)	104.2 (2)	96.3 (2)	97.8 (6)	94.7 (6)	
P(1)-P(4)-C(13)	97.4 (1)	99.1 (3)	103.2 (6)	101.3 (7)	
C(7)-P(4)-C(13)	104.4 (3)	105.7 (3)	102.6 (8)	104.8 (7)	
M-P(4)-C(7)		120.0 (2)	124.1 (5)	125.4 (5)	
M-P(4)-C(13)		113.1 (2)	114.7 (5)	113.3 (6)	
M-P(4)-P(1)		119.65 (9)	111.4 (3)	113.5 (2)	

[a] Values for the analogous bond lengths and angles of $N_3P_3Cl_5Ph$.

of similar length to the corresponding bonds in $N_3P_3Cl_5Ph$. The changes in P–N bond length at increasing distances from the P(1) atom show the "long–short–medium" pattern that has been detected previously in partially alkyl-, aryl-, or transition-metal-substituted cyclotriphosphazenes.[12,14] This has been attributed to differences in the relative electronegativities of the pairs of substituents bound to each phosphorus atom of the phosphazene ring. The phosphorus–nitrogen ring is significantly puckered ($\chi^2 = 2591$ for the weighted least-squares plane through the phosphazene ring). Atom P(3) deviates from the plane of the other five atoms by 0.127 Å. In contrast, the phosphazene ring of $N_3P_3Cl_5Ph$ is only slightly nonplanar ($\chi^2 = 507$). The geometry of the phenyl group attached to the phosphazene ring and the bond lengths and angles of the PCl_2 units are normal.

The length of the P(V)–P(III) bond that binds the phosphino substituent to the phosphazene ring is 2.199 (2) Å. This value is slightly less than that of the P(V)–P(V) bond of the bi(cyclophosphazene) **3**[15] and the P(III)–P(III) bond of P_2Me_4,[16] which have the values 2.208 (3) Å, and 2.212 (1) Å, respectively. In general, the bond lengths and angles of the diphenylphosphino group are comparable to those in PPh_3.[17] Interestingly, however, the P(1)–P(4)–C(13) angle is 97.4 (1)°, approximately 6.8° less than the P(1)–P(4)–C(7) angle.

Synthesis and Characterization of Complexes 5–7. Attempts were made to coordinate both mononuclear and polynuclear transition-metal moieties to the phosphino group of **1**.

The mononuclear transition-metal fragments $Cr(CO)_5$ and $Fe(CO)_4$ were bound to the phosphino group of **1** as follows. UV photolysis of a solution of **1** and $Cr(CO)_6$ in toluene, or reaction of **1** with $Cr(CO)_5(THF)$ in THF, led to the isolation of the pale yellow chromium complex, **5**, in good yield. Reaction of **1** with $Fe_2(CO)_9$, followed by filtration chromatography on silica gel, gave **6** in excellent yield as a yellow solid.

The trinuclear metal fragment $Ru_3(CO)_{11}$ was attached to **1** via the thermal reaction of equimolar amounts of **1** and $Ru_3(CO)_{12}$ in toluene which, after column chromatography, afforded the cluster species **7** as an orange-red solid in moderate yield. The lower yield of **7** compared to **5** and **6** may be attributed to the possibility of multiple substitution. Indeed, in this reaction, although **1** was completely consumed (as deduced by ^{31}P NMR), unreacted $Ru_3(CO)_{12}$ was still isolated. Furthermore, an additional product was isolated as a red-orange solid that showed IR carbonyl bands consistent with the presence of both the di- and trisubstitution products **8** and **9**. The formation of multiply substituted products has important implications for the synthesis of high polymeric analogues of **7**. Such species formed by phosphino groups from adjacent polymer chains would represent cross-link sites and lead to insolubility. Attempts to form the monosubstituted compound **7** exclusively, from equimolar amounts of **1** and $Ru_3(CO)_{12}$ in THF using electron-transfer catalysis[18] with $Na[Ph_2CO]$ as initiator, were unsuccessful. This may be attributed to a reaction between **1** and the benzophenone ketyl radical anion.[19] The structure of compounds **5–7** was studied by a combination of ^{31}P NMR and IR spectroscopy, elemental analysis, and mass spectrometry. Thus, the ^1H-decoupled ^{31}P NMR spectra of **5–7** show two significant differences from that of **1**. First, the doublet of triplets resonance of the diphenylphosphino group appears at

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(19) In a separate experiment **1** was found to react with $Na[Ph_2CO]$ in THF to give a complex mixture of products that could not be identified by ^{31}P NMR spectroscopy.

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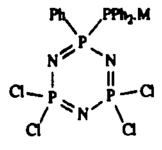

5 M = $Cr(CO)_5$
6 M = $Fe(CO)_4$
7 M = $Ru_3(CO)_{11}$

$(N_3P_3Cl_4PhPPh_2)_nRu_3(CO)_{12-n}$

8 n = 2
9 n = 3

much lower field (55.8 ppm for **5**, 71.7 ppm for **6**, and 33.5 ppm for 7) compared to the high-field shift (−14.0 Hz) characteristic of uncoordinated **1**. Second, the magnitude of the one-bond phosphorus–phosphorus coupling constant ($^1J_{PP}$) is considerably reduced (73 Hz for **5**, 33 Hz for **6**, and 39 Hz for **7** compared to 237 Hz for **1**). The IR spectra of **5**, **6** and **7** showed intense absorptions at ca. 1200 cm^{-1}, which corresponded to P–N stretches, and carbonyl bands. These were consistent with the assigned structures. Interestingly, the carbonyl absorptions of **5–7** occur at slightly higher wavenumbers than those of the analogous triphenylphosphine complexes (Table IV), indicating that **1** is a marginally better π-acceptor ligand than PPh_3. This conclusion is also supported by X-ray diffraction data described in the next section and is consistent with the known electron-withdrawing properties of the phosphazene ring.[22-26]

X-ray Structures of 5 and 7. In order to probe the structural consequences of metal coordination with respect to the phosphazene ring in **1** and to allow a comparison of the ligating ability of **1** with PPh_3, X-ray diffraction studies of the mononuclear complex **5** and the polynuclear species **7** were undertaken.

A summary of cell constants and data collection parameters, and selected bond lengths and angles are given in Tables I and II, respectively. Final fractional atomic coordinates are given in Tables V–VII. The molecular structure of **5** is shown in Figure 2. In the case of **7**, two crystallographically distinct molecules, **7a** and **7b**, were identified, which differed in the orientation of the diphenylphosphino group. These are illustrated in parts a and b of Figure 3, respectively. The X-ray crystal structure determinations confirmed that the phosphino group of **1** is coordinated to a $Cr(CO)_5$ fragment in **5** and a $Ru_3(CO)_{11}$ cluster fragment in **7**. No evidence for coordination to skeletal nitrogen atoms was found in either case. The structure determination of **7** showed that the phosphinophosphazene occupies an equatorial position with respect to the triangle of ruthenium atoms. This is analogous to the substitution pattern observed with PPh_3.[21]

The most significant structural changes following coordination occur in the environment of the phosphorus atom of the phosphino group. In particular, the P–P bond linking the PPh_2 group to the phosphazene ring is lengthened from 2.119 (2) Å in **1** to 2.234 (2) Å in **5**, 2.24 (1) Å in **7a**, and 2.26 (1) Å in **7b**. The geometry of the phosphazene ring is relatively unaltered following coordination, with bond lengths and angles similar to those in **1**.

The lengths of the phosphorus-transition-metal bonds in **5** and **7** are significantly shorter than the values for the analogous PPh_3 complexes. Specifically, the length of the P(4)–Cr bond in **5** is 2.387 (2) Å compared to a P–Cr bond length of 2.422 (1) Å in $Cr(CO)_5PPh_3$).[27] Similarly, the P(4)–Ru bond lengths in **7a** and **7b** are 2.345 (4) and 2.341 (4) Å, respectively, compared to a P–Ru bond length of 2.380 (6) Å in $Ru_3(CO)_{11}PPh_3$.[21] This is consistent with a greater degree of π-back-bonding to the phosphinophosphazene compared with that to PPh_3, as suggested by IR evidence (see the previous section). The geometries of the organometallic fragments in **5**, **7a**, and **7b** are normal.

Table IV. Infrared Carbonyl Spectra for **5–7** and Related Compounds

compd	ν(CO),^{a} cm^{-1}	ref
$N_3P_3Cl_4PhPPh_2{\cdot}Cr(CO)_5$ (**5**)	2068 (m), 1993 (w), 1955 (sh), 1951 (vs)	this work
$Cr(CO)_5(PPh_3)$	2064 (m), 1984 (w), 1945 (vs)	this work
$N_3P_3Cl_4PhPPh_2{\cdot}Fe(CO)_4$ (**6**)	2056 (m), 1985 (m), 1959 (s), 1952 (s)	this work
$Fe(CO)_4(PPh_3)$	2051 (m), 1979 (m), 1945 (s)	20
$N_3P_3Cl_4PhPPh_2{\cdot}Ru_3(CO)_{11}$ (**7**)	2102 (m), 2050 (s), 2038 (m), 2029 sh), sh), 2020 (s), (w), (w), 1990 (br)	this work
$Ru_3(CO)_{11}(PPh_3)$	2097 (7), 2046 (s), 2030 (sh), 2023 (sh), 2014 (s), 1996 (sh), 1986 (m), 1972 (sh), 1960 (sh)	21

^{a} In hexanes solvent.

Table V. Final Fractional Atomic Coordinates for Non-Hydrogen Atoms of **5**

atom	*x*	*y*	*z*
Cr	0.3862 (1)	−0.1001 (1)	0.3593 (1)
Cl(1)	0.1548 (2)	0.0983 (2)	0.5908 (2)
Cl(2)	0.1937 (2)	0.2355 (1)	0.4262 (4)
Cl(3)	0.0212 (1)	0.1490 (1)	0.0474 (3)
Cl(4)	−0.0087 (1)	0.0036 (1)	0.1963 (2)
P(1)	0.2314 (1)	0.0469 (1)	0.2008 (2)
P(2)	0.1664 (1)	0.1286 (1)	0.4007 (2)
P(3)	0.0739 (1)	0.0808 (1)	0.1834 (2)
P(4)	0.2717 (1)	−0.0715 (1)	0.2208 (2)
O(1)	0.2926 (3)	−0.2185 (3)	0.4918 (5)
O(2)	0.3576 (4)	0.0182 (3)	0.5700 (5)
O(3)	0.5263 (3)	−0.1417 (4)	0.5400 (6)
O(4)	0.4310 (3)	−0.2299 (3)	0.1876 (6)
O(5)	0.4909 (3)	0.0039 (3)	0.2113 (6)
N(1)	0.2356 (3)	0.0842 (3)	0.3474 (5)
N(2)	0.0837 (4)	0.1235 (4)	0.3227 (6)
N(3)	0.1465 (3)	0.0454 (3)	0.1250 (5)
C(1)	0.2973 (4)	0.0941 (4)	0.0989 (7)
C(2)	0.3568 (5)	0.1383 (4)	0.1626 (9)
C(3)	0.4080 (5)	0.1752 (5)	0.079 (1)
C(4)	0.3968 (5)	0.1691 (5)	−0.061 (1)
C(5)	0.3400 (6)	0.1257 (5)	−0.1193 (9)
C(6)	0.2872 (5)	0.0875 (4)	−0.0419 (7)
C(7)	0.2679 (4)	−0.0914 (3)	0.0409 (6)
C(8)	0.3375 (4)	−0.0974 (4)	−0.0213 (6)
C(9)	0.3367 (5)	−0.1075 (4)	−0.1599 (7)
C(10)	0.2654 (6)	−0.1134 (5)	−0.2346 (8)
C(11)	0.1964 (5)	−0.1081 (5)	−0.1748 (7)
C(12)	0.1960 (4)	−0.0955 (4)	−0.0339 (6)
C(13)	0.1838 (4)	−0.1132 (3)	0.2813 (6)
C(14)	0.1494 (4)	−0.1770 (4)	0.2245 (7)
C(15)	0.0839 (5)	−0.2066 (4)	0.2794 (9)
C(16)	0.0546 (5)	−0.1743 (4)	0.3949 (8)
C(17)	0.0903 (4)	−0.1136 (4)	0.4523 (7)
C(18)	0.1570 (4)	−0.0812 (4)	0.4003 (7)
C(19)	0.3271 (4)	−0.1720 (4)	0.4432 (6)
C(20)	0.3652 (4)	−0.0243 (4)	0.4866 (7)
C(21)	0.4725 (4)	−0.1251 (4)	0.4713 (7)
C(22)	0.4131 (4)	−0.1791 (4)	0.2477 (7)
C(23)	0.4495 (4)	−0.0331 (4)	0.2676 (8)

Cleavage of the P–P Bond of 1 and 6 by Sodium Trifluoroethoxide. Of crucial importance to the possible extension of the work to the high-polymer level is the stability of the P(V)–P(III) bond that links the phosphino group to the phosphazene ring. The first indication of the lability of this linkage was the air and moisture sensitivity of **1**. Although no intermediates or decomposition products were identified, ^{31}P NMR studies showed clearly a disappearance of the resonances associated with both the phosphino and the phosphino-bearing phosphorus atoms. This was evidence that cleavage of the P–P bond had occurred. The coordination compounds **5–7** show greater stability toward air and moisture, especially in the solid state.

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(24) Allen, C. W. *J. Organomet. Chem.* **1977**, *125*, 215.
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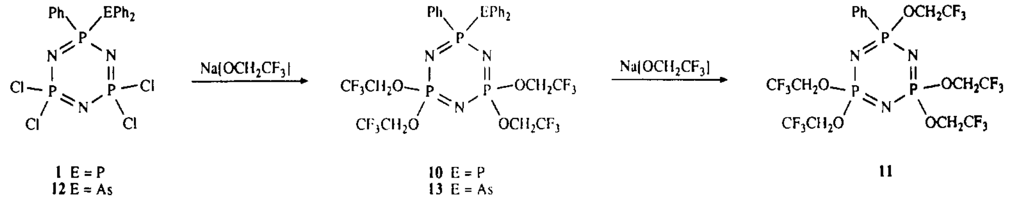
(26) Saraceno, R. A.; Riding, G. H.; Allcock, H. R.; Ewing, A. G. *J. Am. Chem. Soc.* **1988**, *110*, 980.

Scheme II



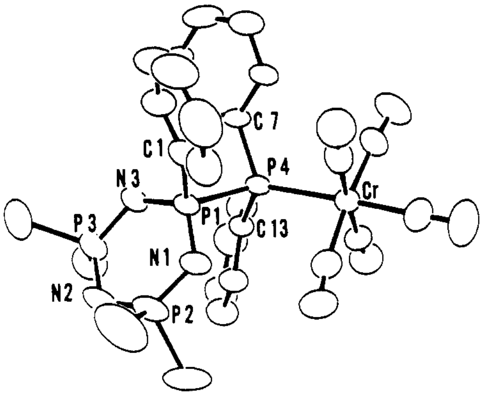


Figure 2. Molecular structure of **5**.

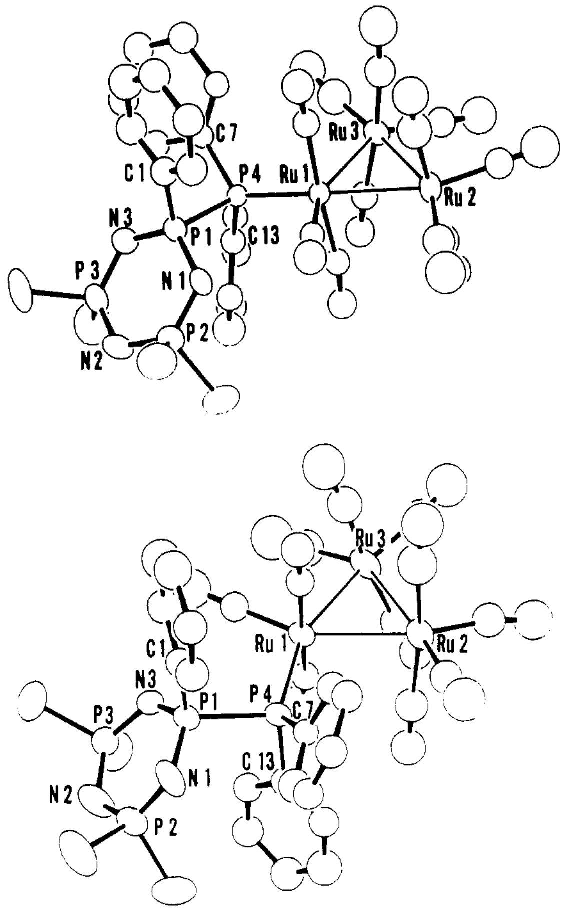


Figure 3. Molecular structure of **7a** (a, top) and **7b** (b, bottom).

In order to investigate the stability of the P–P bond toward nucleophiles, compounds **1** and **6** were allowed to react with sodium trifluoroethoxide, a reagent commonly used in polyphosphazene substitution chemistry. The reaction of **1** with an excess of this reagent at 25 °C proceded initially via replacement of the chlorine atoms by trifluoroethoxy groups. Thus, compound **10** was identified by ^{31}P NMR after 2 h. However, after 24 h, complete P–P bond cleavage had occurred, with the formation of **11** (Scheme II).

Table VI. Final Fractional Atomic Coordinates for Non-Hydrogen Atoms of **7a**

atom	*x*	*y*	*z*
Ru(1)	0.3785 (1)	0.0760	−0.6494 (1)
Ru(2)	0.5332 (2)	0.1131 (1)	−0.4591 (1)
Ru(3)	0.2351 (2)	0.0881 (1)	−0.4931 (1)
Cl(1)	0.4195 (6)	0.1347 (2)	−1.0244 (5)
Cl(2)	0.5706 (6)	0.0626 (2)	−1.0700 (5)
Cl(3)	−0.0650 (8)	0.0796 (3)	−1.1798 (6)
Cl(4)	0.0728 (8)	0.0082 (2)	−1.2441 (4)
P(1)	0.2551 (5)	0.0344 (1)	−0.9222 (3)
P(2)	0.3866 (5)	0.0786 (2)	−1.0391 (4)
P(3)	0.1136 (6)	0.0480 (2)	−1.1313 (4)
P(4)	0.1785 (4)	0.0566 (1)	−0.7921 (3)
O(1)	0.648 (1)	0.0749 (5)	−0.722 (1)
O(2)	0.328 (1)	0.1563 (4)	0.265 (1)
O(3)	0.538 (2)	0.4959 (5)	0.567 (1)
O(4)	0.633 (2)	0.1370 (6)	−0.234 (1)
O(5)	0.388 (1)	0.1917 (5)	−0.512 (1)
O(6)	0.802 (2)	0.1351 (6)	−0.521 (1)
O(7)	0.675 (2)	0.0351 (5)	−0.393 (1)
O(8)	0.083 (1)	0.1542 (4)	−0.634 (1)
O(9)	0.234 (2)	0.1340 (6)	−0.301 (1)
O(10)	0.361 (2)	0.0146 (6)	−0.373 (1)
O(11)	−0.059 (2)	0.0474 (6)	−0.545 (1)
N(1)	0.387 (1)	0.0624 (5)	−0.931 (1)
N(2)	0.252 (2)	0.0709 (6)	−1.139 (1)
N(3)	0.118 (2)	0.0299 (5)	−1.023 (1)
C(1)	0.331 (2)	−0.0112 (6)	−0.872 (1)
C(2)	0.481 (2)	−0.0144 (7)	−0.819 (2)
C(3)	0.538 (2)	−0.0486 (7)	−0.770 (2)
C(4)	0.437 (2)	−0.0795 (7)	−0.780 (2)
C(5)	0.286 (2)	−0.0751 (8)	−0.840 (2)
C(6)	0.234 (2)	−0.0414 (7)	−0.883 (2)
C(7)	0.054 (2)	0.0179 (5)	−0.788 (1)
C(8)	−0.067 (2)	0.0112 (6)	−0.877 (1)
C(9)	−0.148 (2)	−0.0232 (7)	−0.886 (2)
C(10)	0.119 (2)	0.4525 (7)	0.802 (2)
C(11)	0.002 (2)	−0.0420 (7)	−0.713 (2)
C(12)	0.085 (2)	−0.0070 (5)	−0.707 (1)
C(13)	0.050 (2)	0.0947 (5)	−0.855 (1)
C(14)	−0.085 (2)	0.0968 (6)	−0.831 (1)
C(15)	−0.180 (2)	0.1286 (7)	−0.873 (1)
C(16)	−0.142 (2)	0.1536 (7)	−0.941 (2)
C(17)	−0.012 (2)	0.1504 (8)	−0.963 (2)
C(18)	0.084 (2)	0.1213 (6)	−0.920 (1)
C(19)	0.543 (2)	0.0761 (5)	−0.699 (1)
C(20)	0.347 (2)	0.1278 (5)	0.304 (1)
C(21)	0.424 (2)	0.0247 (6)	0.406 (1)
C(22)	0.596 (2)	0.1287 (6)	−0.319 (1)
C(23)	0.439 (2)	0.1613 (7)	−0.497 (2)
C(24)	0.702 (2)	0.1267 (7)	−0.500 (2)
C(25)	0.609 (3)	0.0639 (8)	−0.423 (2)
C(26)	0.147 (2)	0.1283 (6)	−0.585 (1)
C(27)	0.233 (2)	0.1174 (6)	−0.373 (1)
C(28)	0.327 (2)	0.0449 (7)	−0.419 (2)
C(29)	0.057 (3)	0.0648 (8)	−0.528 (2)

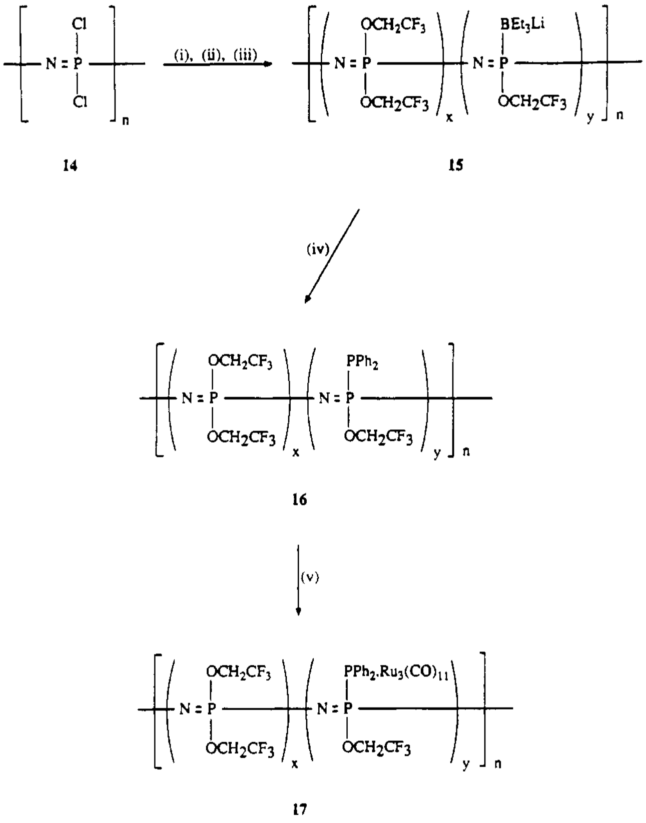
In contrast to **1**, the iron carbonyl complex **6** reacted rapidly to give **11** within 6 h under the same conditions. No intermediate analogous to **10** was identified. This indicated that P–P bond cleavage is more facile in **6** than **1**.

Synthesis, Characterization, and Reactivity of the Arsinophosphazene 12. Because of the lability of the P–P bond of **1**, **5**, **6**, and **7**, we synthesized the analogue of **1** bearing a diphenylarsino substituent in order to determine if the P–As bond would be more stable.

Table VII. Final Fractional Atomic Coordinates for Non-Hydrogen Atoms of **7b**

atom	*x*	*y*	*z*
Ru(1)	0.0692 (2)	0.2869 (1)	0.6119 (1)
Ru(2)	−0.0959 (2)	0.2793 (1)	0.7587 (1)
Ru(3)	0.1994 (2)	0.2502 (1)	0.8078 (1)
Cl(1)	−0.3619 (7)	0.2875 (3)	0.0900 (5)
Cl(2)	−0.2313 (8)	0.3566 (2)	0.0319 (4)
Cl(3)	0.1418 (6)	0.2351 (2)	0.2309 (5)
Cl(4)	0.2745 (6)	0.3099 (2)	0.1811 (4)
P(1)	−0.0301 (5)	0.3333 (1)	0.3403 (3)
P(2)	−0.1789 (6)	0.3197 (2)	0.1312 (4)
P(3)	0.0976 (5)	0.2910 (2)	0.2184 (4)
P(4)	−0.1175 (5)	0.3066 (1)	0.4620 (3)
O(1)	0.032 (2)	0.2027 (5)	0.546 (1)
O(2)	0.345 (2)	0.2859 (6)	0.545 (1)
O(3)	0.147 (2)	0.3683 (4)	0.694 (1)
O(4)	0.058 (2)	0.3455 (6)	0.888 (1)
O(5)	−0.168 (2)	0.2366 (6)	0.935 (1)
O(6)	−0.261 (2)	0.2170 (5)	0.606 (1)
O(7)	0.382 (2)	0.8277 (6)	0.302 (2)
O(8)	0.016 (2)	0.1768 (5)	0.771 (1)
O(9)	0.540 (2)	0.7170 (7)	0.255 (2)
O(10)	0.304 (2)	0.2260 (6)	0.035 (2)
O(11)	0.372 (2)	0.3264 (7)	0.862 (2)
N(1)	−0.164 (2)	0.3425 (4)	0.234 (1)
N(2)	−0.044 (2)	0.2973 (6)	0.122 (1)
N(3)	0.100 (1)	0.3065 (4)	0.325 (1)
C(1)	0.038 (2)	0.3788 (6)	0.394 (1)
C(2)	0.190 (2)	0.3808 (7)	0.452 (2)
C(3)	0.242 (3)	0.4185 (9)	0.502 (2)
C(4)	0.154 (3)	0.4461 (8)	0.490 (2)
C(5)	−0.001 (2)	0.4447 (7)	0.433 (2)
C(6)	−0.053 (2)	0.4083 (7)	0.384 (2)
C(7)	−0.256 (2)	0.3454 (5)	0.457 (1)
C(8)	−0.373 (2)	0.3519 (7)	0.368 (2)
C(9)	−0.455 (2)	0.3839(6)	0.363 (1)
C(10)	−0.429 (2)	0.4105 (6)	0.439 (1)
C(11)	−0.315 (2)	0.4024 (6)	0.536 (1)
C(12)	−0.227 (2)	0.3700 (6)	0.541 (2)
C(13)	−0.228 (2)	0.2671 (6)	0.387 (1)
C(14)	−0.152 (2)	0.2419 (6)	0.341 (1)
C(15)	−0.221 (2)	0.2124 (7)	0.284 (2)
C(16)	0.376 (2)	0.7059 (7)	0.728 (2)
C(17)	−0.449 (3)	0.2313 (8)	0.321 (2)
C(18)	−0.378 (2)	0.2618 (6)	0.378 (2)
C(19)	0.041 (2)	0.2347 (6)	0.575 (1)
C(20)	0.237 (2)	0.2865 (6)	0.570 (1)
C(21)	0.118 (2)	0.3372 (6)	0.665 (1)
C(22)	0.011 (3)	0.3210 (9)	0.837 (2)
C(23)	−0.128 (2)	0.2547 (7)	0.873 (2)
C(24)	−0.195 (2)	−0.2386 (7)	0.663 (2)
C(25)	0.276 (2)	0.8077 (7)	0.284 (2)
C(26)	0.080 (2)	0.2051 (6)	0.779 (2)
C(27)	0.362 (3)	0.2288 (8)	0.766 (2)
C(28)	0.252 (2)	0.2368 (7)	0.952 (2)
C(29)	0.296 (3)	0.2992 (8)	0.846 (2)

Scheme III



(i) 1.8 Na[OCH_2CF_3], (ii) Li[BEt_3H], (iii) Na[OCH_2CF_3]
(iv) PPh_2Cl, (v) $Ru_3(CO)_{12}$

The arsinophosphazene **12**, the first example of a phosphazene with a P–As bond, was synthesized in good yield by the reaction of the chloroarsine $AsPh_2Cl$ with **4**. Compound **12** was studied by ^{31}P NMR spectroscopy, mass spectrometry, and elemental analysis. The ^{31}P NMR spectrum of **12** showed a triplet at 37.8 ppm ($^2J_{PNP}$ = 26 Hz) assigned to the phosphorus atom bearing the diphenylarsino substituent and a doublet at 15.8 ppm ($^2J_{PNP}$ = 26 Hz) assigned to the PCl_2 units. The electron-impact mass spectrum of **12** showed the expected molecular ion (*m/z* 583) and isotope pattern.

Compound **12** was also found to be air- and moisture-sensitive. The reaction of **12** with sodium trifluoroethoxide was also studied in order to provide a comparison of the susceptibilities of the P–As bond of **12** and the P–P bond in **1** toward cleavage by nucleophiles. After treatment of **12** with an excess of sodium trifluoroethoxide at room temperature, compound **13** was identified by ^{31}P NMR after 1 h. The subsequent cleavage of the P–As bond to afford **11** occurred relatively slowly and required 5 days to reach completion (Scheme II). This indicated that the P–As bond of **12** is more resistant to cleavage by trifluoroethoxide ions than the P–P bond of **1**, which required only 24 h to reach completion under the same reaction conditions.

Synthesis of High Polymers Bearing Backbone-Bound Phosphino Groups. Attempts were made to extend the small molecule work described above to the more challenging macromolecular level. In particular, we attempted to synthesize a polymer bearing uncoordinated phosphino groups and to then attach the triruthenium cluster moiety $Ru_3(CO)_{11}$. The pathway employed involved several steps (Scheme III). First, poly(dichlorophosphazene) **14** was allowed to react with 1.8 equiv of sodium trifluoroethoxide to replace most of the chlorine atoms with trifluoroethoxy groups. Second, phosphazene anion sites were generated by reaction of the resulting polymer with lithium triethylborohydride.[14] Third, any remaining chlorine atoms were then replaced by treatment with sodium trifluoroethoxide, affording polymer **15**. In the fourth step, excess PPh_2Cl was added to give polymer **16**, identified in solution by ^{31}P NMR spectroscopy. The ^{31}P NMR spectrum of **16** showed broad doublets centered at 20.4 ppm ($^1J_{PP}$ = 206 Hz) and −19.5 ppm ($^1J_{PP}$ = 206 Hz), assigned to the backbone phosphorus atoms that bear a phosphino group and the phosphino phosphorus atom, respectively. Analogous resonances were observed in the cases of the small molecule compounds **1** and **10**. An intense resonance at −8.2 ppm was also detected and was assigned to backbone phosphorus atoms that bear two trifluoroethoxy substituents. In the final step, polymer **16** was treated with $Ru_3(CO)_{12}$ to afford a solution of **17** (identified by ^{31}P NMR). In this step a large excess of the triruthenium cluster was used to prevent multiple substitution by phosphino groups from different polymer chains, which would lead to cross-linking and insolubilization.

The ^{31}P NMR spectrum of **17** showed that the resonances characteristic of the backbone-bound phosphino group of **16** had disappeared and that a single, new broad resonance at 33.2 ppm had emerged. By analogy with the ^{31}P NMR spectrum of the small molecule compound **7**, this may be assigned to coincident resonances of the phosphorus atoms of the phosphino groups and those bearing them. However, attempts to isolate **17** (and also **16**) were unsuccessful. The products proved to be insoluble in all common organic solvents. By analogy with the small molecule chemistry described above, it appears that this instability is probably a consequence of the lability of the P–P bond that binds the phosphino group to the polymer backbone.

Experimental Section

Materials. Species $[NPCl_2]_3$ (provided by Ethyl Corp.) and $Cr(CO)_6$ (Strem) were purified by vacuum sublimation before use. Compounds $Fe_2(CO)_9$ (Strem), $Ru_3(CO)_{12}$ (Strem), PPh_2Cl (Aldrich), and $AsCl_3$ (Strem) were used as received. $Cr(CO)_5(THF)$,[28] $Cr(CO)_5(PPh_3)$,[27] and $[N_3P_3Cl_4Ph]_2$[29] were prepared as described elsewhere. $AsPh_2Cl$ was prepared[30] by the reaction of 2 equiv of PhMgCl (Aldrich) with $AsCl_3$ in THF and was purified by vacuum distillation. All reactions and manipulations were carried out under an atmosphere of dry argon by using standard Schlenk techniques or an inert-atmosphere glovebox (Vacuum Atmospheres). Solvents were dried by standard methods, distilled, and stored over activated 4-Å molecular sieves.

Equipment. UV photolysis was carried out with Pyrex-filtered radiation from a 450-W Canrad-Hanovia lamp. ^{31}P NMR spectra were recorded with the use of either a JEOL FX 90Q instrument operating at 32 MHz or a Bruker AM 300 instrument operating at 120 MHz. Positive chemical shifts were defined as downfield from the shift of external 85% phosphoric acid. Infrared spectra were recorded on a Perkin-Elmer 1710 Fourier transform instrument. Electron-impact mass spectra were obtained with the use of a KRA TOS MS9/50 spectrometer. Elemental microanalyses were obtained by Galbraith Laboratories, Knoxville, TN.

Synthesis of $N_3P_3Cl_4PhPPh_2$ (1). To a suspension of **3** (3.95 g, 5.6 mmol) in THF (60 mL) was added slowly and dropwise a 1.0 M solution of $Li[BEt_3H]$ (11.4 mL, 11.4 mmol) in the same solvent. Hydrogen was evolved, and a homogeneous solution formed. After 1 h, analysis by ^{31}P NMR showed that the phosphazene anion **4** had been generated quantitatively. To this solution was added slowly and dropwise PPh_2Cl (2.44 g, 11.0 mmol) in THF (20 mL), and the reaction mixture was stirred for 2 h. Solvent removal followed by extraction of the residue with toluene (150 mL) and filtration (to remove LiCl) gave a clear solution. The solvent was again removed and the residue dissolved in CH_2Cl_2–hexane (1:4). Cooling to −20 °C for 24 h gave colorless crystals of **1** (4.97 g, 83%).

For **1**: ^{31}P NMR δ 37.9 (dt, $^1J_{PP} = 237$ Hz, $^2J_{PNP} = 18$ Hz), 16.3 (dd, $^2J_{PNP} = 18$ Hz, $^3J_{PPNP} = 9$ Hz), −14.0 (dt, $^1J_{PP} = 237$ Hz, $^3J_{PPNP} = 9$ Hz) ppm; MS theory *m/z* 539, found *m/z* 539. Anal. Calcd: C, 40.10; H, 2.81; N, 7.80. Found: C, 40.43; H, 2.86; N, 7.87.

Synthesis of $N_3P_3Cl_4PhPPh_2{\cdot}Cr(CO)_5$ (5). Method A. A solution of **1** (0.92 g, 1.71 mmol) and excess $Cr(CO)_6$ (1.40 g, 6.36 mmol) in toluene (150 mL) was irradiated with UV light for 18 h. Solvent removal followed by extraction with CH_2Cl_2 (30 mL) and filtration through silica gel (10 cm) gave a pale yellow filtrate. After removal of the solvent, unreacted $Cr(CO)_6$ was removed over 24 h by vacuum sublimation (50 °C, 1×10^{-3} mmHg). Recrystallization from CH_2Cl_2–hexane gave **5** as a pale yellow solid, yield 0.94 g (76%).

Method B. To a solution of **1** (0.77 g, 1.43 mmol) in THF (20 mL) was added an orange solution of $Cr(CO)_5(THF)$ (2.21 mmol) in the same solvent (15 mL). After 2 h of reaction, solvent removal followed by purification as described above gave **5**, yield 0.80 g (77%).

For **5**: ^{31}P NMR δ 55.8 (dt, $^1J_{PP} = 73$ Hz, $^3J_{PPNP} = 6$ Hz), 32.5 (dt, $^1J_{PP} = 73$ Hz, $^2J_{PNP} = 14$ Hz), 17.6 (dd, $^2J_{PNP} = 14$ Hz, $^3J_{PPNP} = 6$ Hz) ppm; MS theory *m/z* 729, found *m/z* 729. Anal. Calcd: C, 37.78; H, 2.07; N, 5.75. Found: C, 37.58; H, 1.95; N, 5.88.

Synthesis of $N_3P_3Cl_4PhPPh_2{\cdot}Fe(CO)_4$ (6). To a solution of **1** (0.81 g, 1.5 mmol) in toluene (20 mL) was added $Fe_2(CO)_9$ (0.60 g, 1.65 mmol). After 4 h of reaction, the brown solution was filtered through silica gel (5 cm) and the bright yellow filtrate was evaporated to dryness. Recrystallization from CH_2Cl_2–hexanes gave **6** as a yellow solid (0.95 g, 90%).

For **6**: ^{31}P NMR δ 71.7 (dt, $^1J_{PP} = 33$ Hz, $^3J_{PPNP} = 6$ Hz), 32.5 (dt, $^1J_{PP} = 33$ Hz, $^2J_{PNP} = 12$ Hz), 18.7 (dd, $^2J_{PNP} = 12$ Hz, $^3J_{PPNP} = 6$ Hz) ppm; MS theory *m/z* 707, found *m/z* 651 ($M^+ - 2CO$). Anal. Calcd: C, 37.36; H, 2.19; N, 5.94. Found: C, 37.02; H, 2.28; N, 5.48.

Synthesis of $N_3P_3Cl_4PhPPh_2{\cdot}Ru_3(CO)_{11}$ (7). A solution of **1** (0.32 g, 0.59 mmol) and $Ru_3(CO)_{12}$ (0.38 g, 0.59 mmol) in toluene (30 mL) was heated at 70 °C for 1 h. To the red solution was added silica (10 g), and the solvent was removed under vacuum. The dry residue was then transferred to a medium-size (2.5 × 30 cm) silica gel–hexanes column. Elution with hexanes gave a yellow band identified by IR spectroscopy as unreacted $Ru_3(CO)_{12}$ (0.09 g, 24%). With CH_2Cl_2–hexanes (1:9), an orange band eluted which, after recrystallization from toluene–hexanes, yielded orange-red crystalline **7** (0.28 g, 41%). Further elution with CH_2Cl_2–hexanes (2:3) gave an orange-red band from which an orange crystalline solid was isolated (0.14 g). The IR spectrum of this product suggested the presence of the di- and trisubstitution products **8** and **9**.

For **7**: ^{31}P NMR δ 33.5 (dt, $^1J_{PP} = 39$ Hz, $^3J_{PPNP} = 8$ Hz), 30.6 (dt, $^1J_{PP} = 39$ Hz, $^2J_{PNP} = 14$ Hz), 17.2 (dd, $^2J_{PPP} = 14$ Hz, $^3J_{PPNP} = 8$ Hz) ppm; MS theory *m/z* 1150, found *m/z* 1150. Anal. Calcd for **6**·0.5(toluene): C, 32.62; H, 1.60; N, 3.51. Found: C, 32.59; H, 1.65; N, 3.70.

For a mixture of **8** and **9**: IR (CH_2Cl_2) $\nu(CO)/cm^{-1}$ 2082 m, 2060 w, 2050 w, 2033 s, 2020 w, 2003 vs, 1985 sh, 1955 br, $\nu(PN)/cm^{-1}$ 1205 vs, br.

Synthesis of $N_3P_3Cl_4PhAsPh_2$ (12). To a stirred suspension of **3** (1.01 g, 1.4 mmol) in THF (10 mL) was added slowly and dropwise 1.0 M $Li[BEt_3H]$ (2.8 mL, 2.8 mmol). After 1 h, the reaction mixture was cooled to 0 °C and a solution of $AsPh_2Cl$ (0.74 g, 2.8 mmol) in THF (10 mL) added over a period of 15 min. After 2 h of reaction, the solvent was removed and the residue extracted with toluene (50 mL). After filtration, the solvent volume was reduced in vacuo to 5 mL, and hexanes (20 mL) were added. Cooling to −55 °C for 48 h gave white crystalline **12**, yield 1.18 g (71%).

For **12**: ^{31}P NMR δ 37.8 (t, $^2J_{PNP} = 25$ Hz), 15.6 (d, $^2J_{PNP} = 25$ Hz) ppm; MS theory *m/z* 583, found *m/z* 583. Anal. Calcd for **12**: C, 37.08; H, 2.60; N, 7.21. Found: C, 36.55; H, 2.38; N, 7.09.

Reactions of 1, 6, and 12 with Sodium Trifluoroethoxide. These reactions were all carried out in the same manner, and the following procedure is typical. A solution of sodium trifluoroethoxide was prepared from sodium (0.20 g, 8.6 mmol) and a deficiency of trifluoroethanol (0.6 g, 6.0 mmol) in THF (10 mL). The solution was filtered and then added slowly to **1** (0.20 g, 0.4 mmol) in THF (5 mL) at 25 °C. After 2 h, **10** had formed almost quantitatively as determined by ^{31}P NMR. After 24 h, reaction, analysis by ^{31}P NMR showed that **11** had formed. To the reaction mixture was added $SiMe_3Cl$ (2 mL) to destroy excess sodium trifluoroethoxide. The solvent was removed and the residue extracted with CH_2Cl_2 (20 mL). Following filtration through silica gel (5 cm), the clear solution was concentrated and then diluted with hexane. Reduction of the solvent volume followed by cooling to −55 °C gave **11** as a colorless oil (0.15 g, 58%).

For **10**: ^{31}P NMR δ 37.1 (dt, $^1J_{PP} = 209$ Hz, $^2J_{PNP} = 14$ Hz), 14.1 (dd, $^2J_{PNP} = 14$ Hz, $^3J_{PNPP} = 8$ Hz), −14.9 (dt, $^1J_{PP} = 209$ Hz, $^3J_{PPNP} = 8$ Hz) ppm.

For the characterization of **11**, see ref 31.

The analogous reaction with **6** gave **11** directly; no intermediates were identified. The reaction with **12** gave the intermediate **13** after 1 h and **11** after 5 days.

For **13**: ^{31}P NMR δ 37.1 (t, $^2J_{PNP} = 8$ Hz), 13.5 (d, $^2J_{PNP} = 8$ Hz) ppm.

Synthesis of $[NP(OCH_2CF_3)_{1.83}(PPh_2)_{0.17}]_n$ (16). To a cooled (0 °C) mechanically stirred solution of **14** (2.1 g, 18.1 mmol) in THF (150 mL) was added slowly and dropwise sodium trifluoroethoxide prepared from sodium (1.5 g, 65.2 mmol) and trifluoroethanol (3.3 g, 33.0 mmol) in the same solvent (80 mL). The reaction mixture was allowed to warm to room temperature and was stirred overnight. A solution of $Li[BEt_3H]$ (8.4 mL, 8.4 mmol, 1.0 M in THF) was then added via syringe. After 4 h, a further quantity of sodium trifluoroethoxide (4.2 mmol) in THF (10 mL) was added and the reaction mixture was stirred for 3 h. Excess PPh_2Cl (2.6 g, 11.9 mmol) was then added via syringe. After 2 h, the ^{31}P NMR spectrum indicated that **16** had formed. An attempted isolation by concentration of the solution and precipitation into hexane (500 mL) resulted in decomposition to a white insoluble material.

For **16**: ^{31}P NMR δ 20.4 (d, $^1J_{PP} = 206$ Hz, half-height peak width 46 Hz), −8.2 (s, half-height peak width 92 Hz), −19.5 (d, $^1J_{PP} = 206$ Hz, half-height peak width 46 Hz) ppm. Integration gave the approximate composition indicated.

Synthesis of $[NP(OCH_2CF_3)_{1.83}\{PPh_2{\cdot}Ru_3(CO)_{11}\}_{0.17}]_n$ (17). To a solution of polymer **16** (4.3 mmol) in THF (50 mL) was added $Ru_3(CO)_{12}$ (2.3 g, 3.6 mmol, 10 equiv/PPh_2 group), and the reaction mixture was heated under gentle reflux for 1.5 h. After the mixture was cooled to room temperature, a ^{31}P NMR spectrum provided evidence that **17** had formed. The reaction mixture was filtered, and the solvent volume was reduced under vacuum. Precipitation into hexanes (500 mL) gave a

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brown material that proved to be insoluble in all common organic solvents.

For **17**: ^{31}P NMR δ 33.2 (s, half-height peak width 92 Hz), −8.1 (s, half-height peak width 126 Hz) ppm.

X-ray Structure Determination Technique. Our general technique is described elsewhere[14] and only details related to the present work will be given here. Crystals of **1** were grown by the slow diffusion of hexanes into a toluene–hexanes solution of **1** at −20 °C. Crystals of **4** and **6** were obtained by cooling toluene–hexanes solutions to −20 °C. A summary of the important crystallographic data is presented in Table I.

The structures were solved by a combination of direct methods (using MULTAN 82[32]) and Fourier methods. All structures were refined by full-matrix, least-squares calculations with anisotropic thermal parameters for the non-hydrogen atoms except for **7** in which the O, N, and C atoms were refined isotropically. In the case of **1**, difference Fourier syntheses, calculated toward the end of refinement, showed maxima consistent with the expected positions of H atoms. These H atoms were included in the refinement.

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Supplementary Material Available: Figures showing crystal structures for **1**, **5**, and **7** with complete labeling of non-hydrogen atoms and tables giving complete positional and thermal parameters, bond lengths, bond angles, and anisotropic thermal parameters for **1**, **5**, and **7** and hydrogen atom coordinates for **1** (41 pages); tables of calculated and observed structure factors for **1**, **5**, and **7** (109 pages). Ordering information is given on any current masthead page.

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Synthesis, Spectroscopic Studies, and Structure of an Unusual Dirhenium Complex with a Bridging Hydride Ligand

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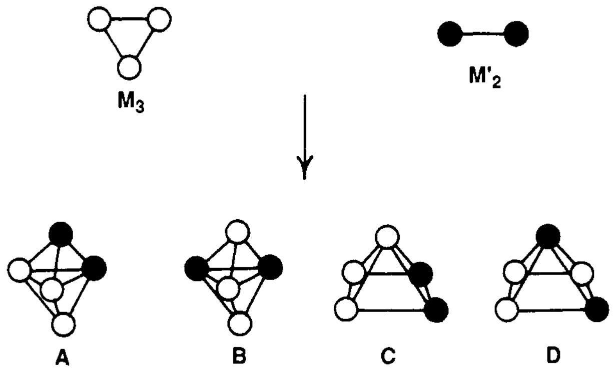
The preparation and characterization of an unusual dirhenium hydrido–carbonyl compound is described. The product has been accessed by several methods, including the reaction of $Re_2Cl_4(\mu\text{-dppm})_2$ with various carbonyl clusters in the presence of H_2 and the direct combination of the starting material with an H_2/CO gas mixture in refluxing toluene. Details of these and other syntheses are presented. Compound **1**, $Re_2(\mu\text{-Cl})(\mu\text{-H})Cl_2(CO)_2(dppm)_2$, crystallizes in the tetragonal space group $P4_12_12$ with unit cell dimensions a = 14.935 (2) Å, b = 14.935 (2) Å, c = 25.804 (2) Å, V = 5755 (4) Å^3, and Z = 4. The structure was refined to least-squares residuals of R = 0.0304, R_w = 0.0368 and quality-of-fit 0.643. The molecules reside on crystallographic 2-fold axes, and the asymmetric unit is defined by half of a formula unit. The binuclear structure consists of two trans diphosphine ligands bisecting an equatorial plane that contains one bridging and two terminal chloride ligands on the same side of the molecule as well as two terminal carbonyl ligands. The bridging hydride ligand, although not located in the X-ray refinement, is postulated on the basis of detailed ^1H NMR studies and is further substantiated by the diamagnetism of the compound. The μ-H resonance is quite unusual with a chemical shift of δ = +12.75 ppm in CD_2Cl_2. The presence of the μ-H ligand leads to the formulation of **1** as a molecule possessing an Re_2^{4+} core with an edge-sharing bioctahedral geometry. Both the Re–Re distance of 2.605 (1) Å and the electrochemistry of the new compound ($E_{p,c}$ = +1.47, $E_{1/2}(ox)$ = +0.63, $E_{1/2}(red)_1$ = −0.73, and $E_{1/2}(red)_2$ = −1.44 V vs Ag/AgCl) are very similar to that which has been reported for other dirhenium M_2L_{10} systems containing a mixture of chloride, phosphine, and carbonyl ligands. This point is discussed along with other pertinent structural data. In addition to an X-ray study, the new compound was characterized by elemental analysis, infrared spectroscopy, FAB mass spectrometry, ^1H and ^{31}P NMR spectroscopy, and cyclic voltammetry.

We are currently investigating reactions between various coordinatively unsaturated binuclear compounds and trinuclear carbonyl complexes. In addition to the likelihood of formation of tetra- or pentanuclear mixed-metal clusters by this approach,[1-10] as in Scheme I, there is also a possibility that interesting homometallic products resulting from ligand exchange may be isolated.[11] In a recent paper by Shore and co-workers, the former result was realized in the case of the reaction between $(\mu\text{-H})_2Os_3(CO)_{10}$ and $[(\eta^5\text{-}C_5H_5)Mo(CO)_n]_2$ (n = 2, 3) under a hydrogen atmosphere to form $(\mu\text{-H})_2(\eta^5\text{-}C_5H_5)_2Mo_2Os_3(CO)_{12}$.[8] This novel pentanuclear cluster is derived from a formal addition of the Mo–Mo dimer to an edge of the Os_3 unit with retention of the Mo–Mo bond (structure B in Scheme I). This synthetic approach had previously been studied by Curtis and co-workers, but evidently no reaction occurred in the absence of H_2.[12]

Scheme I. Pentanuclear Cluster Frameworks Derived from Trinuclear (M_3) and Binuclear (M'_2) Fragments



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