+ H_2 mixture. In the presence of metallic or zerovalent ruthenium atoms, CO ligands from the neighboring $Ru(CO)_2$ species can easily migrate to the free ruthenium sites, on which they dissociate and form methane.

The metallic ruthenium site is also a center for hydrogen dissociation and is a necessary requirement for the methanation reaction.

When decomposition takes place at high temperature (up to 773 K), all CO ligands which were required to stabilize single ruthenium atoms in dicarbonyl species are removed and the ruthenium particles tend to migrate on the surface to form large aggregates. On large particles the mode of CO chemisorption is changed; in particular, only a negligible amount of dicarbonyl species is produced.

In conclusion, it can be established that free ruthenium sites are a necessary requirement for the CO hydrogenation reaction. Initially, the presence of dicarbonyl species in the temperature range in which the reaction takes place is important to stabilize the high dispersion of ruthenium. As soon as free ruthenium sites are also present, the CO molecules from the ruthenium dicarbonyl species indicated by the IR bands at 2072 and 2001 cm^{-1} easily migrate to the free ruthenium sites due to their high mobility and react with hydrogen to produce methane. Since these molecules are already in an activated form, it explains their higher reactivity compared to those chemisorbed from the gas phase, i.e. ^{13}CO. This ultimately leads to the initial $^{12}CH_4$ formation when H_2 + ^{13}CO is used.

Registry No. $Ru_3(CO)_{12}$, 15243-33-1; $Ru(CO)_2$, 106960-32-1; Ru, 7440-18-8; CH_4, 74-82-8; $H_3C(CH_2)_3CH_3$, 109-66-0.

Contribution from the Department of Chemistry,
The Pennsylvania State University, University Park, Pennsylvania 16802

Cyclotriphosphazenes with Geminal (Trimethylsilyl)methyl and Alkyl or Aryl Side Groups[1]

Harry R. Allcock,* David J. Brennan, Beverly S. Dunn, and Masood Parvez

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The synthesis of a series of organosilyl cyclophosphazenes of formula *gem*-$N_3P_3Cl_4(CH_2SiMe_3)(R)$, where R = C_2H_5, *i*-C_3H_7, *n*-C_4H_9, *t*-C_4H_9, *neo*-C_5H_{11}, and C_6H_5, via organometallic reactions, is described. The chlorine atoms in the cyclic trimers were replaced by trifluoroethoxy groups by reactions that led to either retention of the (trimethylsilyl)methyl units or replacement of them by methyl groups, depending on the reaction conditions. The crystal and molecular structures of *gem*-$N_3P_3Cl_4(CH_2SiMe_3)(t\text{-}C_4H_9)$ and the related derivative *gem*-$N_3P_3Cl_4(CH_2SiMe_3)_2$ were determined by single-crystal X-ray diffraction methods. Steric hindrance involving the organosilyl units results in a widening of the external angle at the supporting phosphorus atom and a narrowing of the corresponding ring angle at that site. Crystals of *gem*-$N_3P_3Cl_4(CH_2SiMe_3)(t\text{-}C_4H_9)$ are orthorhombic with space group *Pbca*, with a = 14.884 (4) Å, b = 15.815 (4) Å, c = 16.615 (4) Å, V = 3910.9 Å^3, and Z = 8. Crystals of *gem*-$N_3P_3Cl_4(CH_2SiMe_3)_2$ are monoclinic with space group $P2_1/n$, with a = 10.145 (4) Å, b = 11.060 (5) Å, c = 19.999 (6) Å, β = 103.56 (3)°, V = 2181.4 Å^3, and Z = 4.

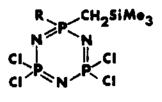
Introduction

Cyclic and linear high-polymeric phosphazenes are now known that bear a wide variety of inorganic, organic, or organometallic side groups.[2,3] A recent development has been the synthesis of phosphazenes with organosilicon side units.[4-7] At the high-polymeric level[6] these species are hybrid systems with characteristics that resemble those of both poly(organophosphazenes) and poly(organosiloxanes).

The main method for the preparation of phosphazene high polymers involves the ring-opening polymerization of small-molecule cyclic phosphazenes. Thus, the synthesis of phosphazene cyclic trimers or tetramers that bear organosilicon side groups is an essential first step in the assembly of hybrid organosilicon-organophosphazene macromolecules. A second reason for the study of small-molecule phosphazene ring systems is that they provide excellent reaction models for the more complex substitution reactions carried out on the corresponding high polymers. The small-molecule cyclic species also provide structural models for the high polymers since their molecular geometries can be deduced more easily by X-ray diffraction techniques.

In earlier work[5] at the cyclic trimer level, we developed a series of organometallic pathways that allowed access to small-molecule cyclotriphosphazenes with siloxane or (trimethylsilyl)methyl units linked to the phosphazene ring. In several cases, two identical organosilicon units were attached to one skeletal phosphorus atom. In other examples, a ring phosphorus atom bore one organosilicon unit and either a chlorine atom or a methyl group. The remaining four side groups were either chlorine atoms or trifluoroethoxy groups introduced by nucleophilic replacement of chlorine.

In the present work, we have extended the number of accessible structures to the 12 compounds depicted as species **1a–f** and **2a–f**. The compounds of formula **1** and **2**, where R = CH_3, were reported earlier.[5] Species **3a–f** are compounds formed during the conversion of **1** to **2** by a pathway that will be discussed.



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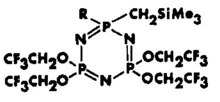

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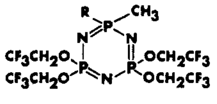

3

a	R = C_2H_5
b	*i*-C_3H_7
c	*n*-C_4H_9
d	*t*-C_4H_9
e	*neo*-C_5H_{11}
f	C_6H_5

In this study, we have attempted to answer the following questions: (a) What reaction pathways are available for the sequential replacement of two chlorine atoms in hexachloro-

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(1) This is the fourth paper from our laboratory on organosilicon-organophosphazene chemistry. For the first three papers, see ref 4–6.

(2) Allcock, H. R. *Phosphorus-Nitrogen Compounds*; Academic: New York, 1972.

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(6) Allcock, H. R.; Brennan, D. J.; Graaskamp, J. M. *Macromolecules* **1988**, *21*, 1.

(7) Wisian-Neilson, P.; Neilson, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 2848.

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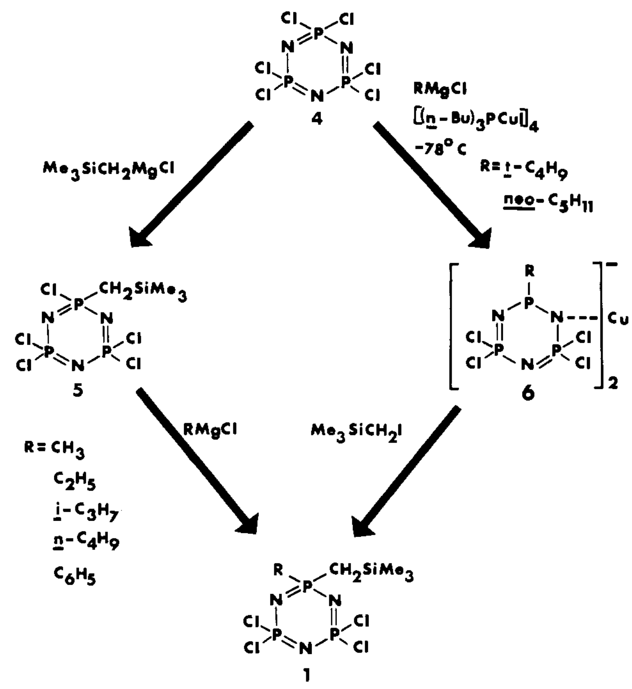
Scheme I



cyclotriphosphazene (**4**) by the organosilyl group and the organic unit and, in particular, which substituent group should be introduced first? (b) What reaction conditions are needed to allow the chlorine atoms in **1** to be replaced by trifluoroethoxy groups without cleavage of the CH_2–Si bonds? This question is of particular importance with respect to the replacement of chlorine atoms by organic units in the corresponding linear high polymers. (c) Do organosilyl cyclophosphazenes possess any structural peculiarities that might influence their thermal stability, their polymerization behavior, or their reactivity?

In the following sections, we discuss first the organometallic pathways used for the synthesis of species **1**, followed by the behavior of these species in the presence of trifluoroethoxide ion and the characterization of the products by microanalytical, mass spectrometric, and NMR methods. Finally, the results of two single-crystal X-ray structure determinations are discussed.

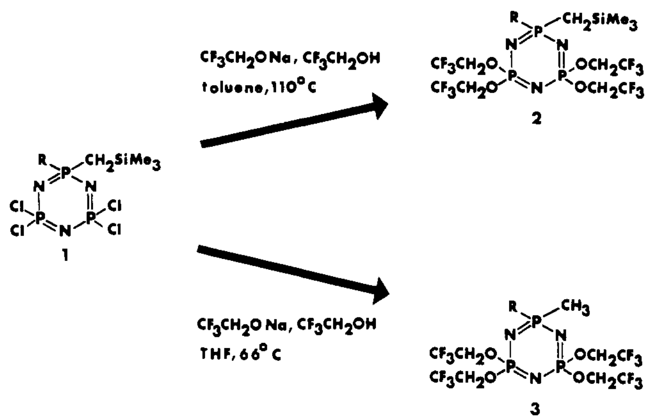
Results and Discussion

Synthesis of Chlorocyclophosphazenes 1a–f. As shown in earlier work,[5] hexachlorocyclotriphosphazene (**4**) reacts with ((trimethylsilyl)methyl)magnesium chloride to yield species **5** (Scheme I). Compound **5** was found in the earlier study to react with methylmagnesium chloride to replace the geminal chlorine atom by a methyl group. In the present work, we have shown that **5** reacts in a similar manner with ethyl-, isopropyl-, *n*-butyl-, or phenylmagnesium chloride to yield the geminally disubstituted species **1a–c** and **1f** in moderate to high yields (see Table I). Further halogen replacement appeared to be difficult under these reaction conditions.

However, the *tert*-butyl and neopentyl derivatives, **1d,e**, could not be prepared by this route. Instead, compound **4** was converted to an organocopper intermediate, **6**, by reaction with *tert*-butyl-[8] or neopentylmagnesium chloride[6] in the presence of the tributylphosphine complex of copper iodide. Species **6** then reacted with (trimethylsilyl)methyl iodide to give the appropriate geminally disubstituted species, **1d,e**.

Replacement of the Chlorine Atoms in 1 by Trifluoroethoxy Groups. The replacement of chlorine atoms in hexachlorocyclotriphosphazene (**4**) by reaction with sodium trifluoroethoxide is one of the best known and longest established methods for the conversion of a hydrolytically unstable chlorocyclophosphazene to a hydrolytically stable derivative.[9] The same substitution reaction was used to prepare the first stable high-polymeric phosphazene from poly(dichlorophosphazene).[10,11] This reaction is, therefore, of considerable significance whenever hydrolytic stability in phosphazenes is an important consideration.

Scheme II



Treatment of the six compounds of formula **1** with excess sodium trifluoroethoxide resulted in a clean replacement of chlorine by trifluoroethoxy to yield species **2**, *provided* toluene was used as a reaction solvent at 110 °C. However, if a more polar solvent, such as THF, is used even at lower temperatures, chlorine replacement is accompanied by CH_2–Si bond cleavage and the replacement of a (trimethylsilyl)methyl unit by a methyl group. These two pathways are summarized in Scheme II. These alternative pathways were detected in earlier work, when phosphazene cyclic trimers with a chloro or methyl group geminal to a (trimethylsilyl)methyl unit were treated with trifluoroethoxide ion.[5] The present work indicates that the presence of bulkier organic groups at the geminal site in no way changes this pattern. Thus, solvent polarity has a much more profound influence on this mechanism than does the steric size or electron-directing influence of the group at the geminal position. It is assumed that sodium trifluoroethoxide is more ionized in THF than in toluene and that the trifluoroethoxide ion is, therefore, more active in nucleophilic attack on silicon. The methyl group in the final product is formed by protonation of the $P–CH_2^-$ residue left after carbon–silicon bond cleavage.

Properties and Characterization of Species 1–3. Species of formula **1** are stable in the absence of moisture. All six compounds are colorless crystalline solids (Table I). Replacement of the chlorine atoms in **1** to yield species **2** yielded compounds that were stable to water. However, the trifluoroethoxy groups lowered the melting points markedly, in some cases to below room temperature (Table I). Compounds of structure **3** are low-melting solids or oils that are stable to moisture.

The structural characterization data are listed in Tables I–III. In each case, the elemental analysis, mass spectrometric, infrared, and NMR data were compatible with the proposed structures. The nonsilylated products (**3**) were also identified by comparisons with the same compounds prepared by the reaction of trifluoroethoxide with *gem*-$N_3P_3Cl_4(CH_3)R$, obtained from previous studies.[6,12,13]

X-ray Crystal Structures. X-ray crystal structure determinations have been carried out on the two compounds depicted as **1d** and **7**. Species **7** was prepared in earlier work.[5] It provides a comparison between the structural influences of *tert*-butyl and (trimethylsilyl)methyl groups on a geminal (trimethylsilyl)methyl unit.

The molecular structures of **1d** and **7** are shown in Figures 1 and 2, respectively. Bond lengths (Tables IV and V), bond angles

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(8) Allcock, H. R.; Harris, P. J. *J. Am. Chem. Soc.* **1979**, *101*, 6221.
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(10) Allcock, H. R.; Kugel, R. L. *J. Am. Chem. Soc.* **1965**, *87*, 4216.
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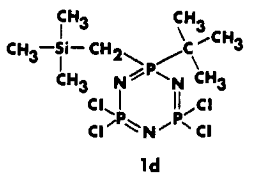
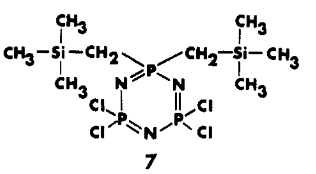


1d



7

(Tables VI and VII), and positional parameters (Tables VIII and IX) for the two compounds are also given.

The most significant features of the molecular structures of **1d** and **7** are the wide exocyclic C–P(1)–C bond angles in both compounds, which undoubtedly reflect steric repulsions between the geminal organic/organometallic side groups. This angle is 108.85 (9)° in **1d** and 107.9 (1)° in **7**. Both are significantly wider than the angle of 101.4 (2)° found for the Cl–P–Cl angles in $(NPCl_2)_3$,[14] and both are wider than the average Cl–P–Cl angles in **1d** [99.59 (3)°] and **7** [100.1 (2)°].

This widening of the exocyclic angle at P(1) becomes translated into a narrowing of the internal (ring) angle at that same atom. Thus, the ring angles in **1d** and **7** are 113.94 (7) and 113.09 (8)°, respectively. These can be compared to the value of 118.4 (1)° found for $(NPCl_2)_3$.[14] Such a narrow ring angle at P(1) inevitably results in a puckering of the phosphazene ring and a separation of the skeletal bonds into unequal lengths. In **1d** the ring is moderately puckered in a chair conformation. Specifically, a plane passes through P(2), P(3), N(1), and N(3), while P(1) and N(2) deviate from this plane by 0.111 (1) and –0.087 (3) Å, respectively. In **7**, the ring is even more highly puckered in a chair distortion, with P(1) and N(2) deviating from the plane of the other four skeletal atoms by 0.163 (1) and –0.152 (2) Å, respectively. In **1d**, the two longest skeletal bonds [average 1.620 (1) Å] are connected to P(1), the shortest [average 1.551 (1) Å] are N(1)–P(2) and N(3)–P(3), and the two bonds furthest from P(1) have an average length of 1.575 (5) Å. A similar pattern is found in **7**. Other examples of this type of ring distortion are known.[13,15–18]

Experimental Section

Materials. Hexachlorocyclotriphosphazene was kindly provided by Ethyl Corp. and was recrystallized from hexane and sublimed at 50 °C/0.05 mmHg. (Chloromethyl)trimethylsilane was obtained from Petrarch Systems, Inc., and was dried over molecular sieves before use. Neopentyl chloride was obtained from Alfa Products and was used as received. The Grignard reagents CH_3MgCl, C_2H_5MgCl, *i*-C_3H_7MgCl, *n*-C_4H_9MgCl, *t*-C_4H_9MgCl, and C_6H_5MgCl were obtained from Alfa Products as 2–3 M solutions in THF. Neopentylmagnesium chloride was prepared by a previously described procedure.[6] (Iodomethyl)trimethylsilane was prepared by the reaction of (chloromethyl)trimethylsilane with sodium iodide in acetone.[19] Methyl iodide was obtained from Aldrich and was used as received. Trifluoroethanol (Halocarbon Products) was dried over 3-Å molecular sieves before use. The reagent $[(n\text{-}Bu)_3PCuI]_4$ was prepared by standard methods.[20] Resublimed magnesium was obtained from Alfa Products and was used as received. Sodium hydride (Aldrich) was washed several times with dry THF to remove mineral oil and was stored in a drybox before use. Tetrahydrofuran (THF) and toluene were dried over sodium benzophenone ketyl and were distilled under an atmosphere of dry nitrogen before use. All reactions were carried out under an atmosphere of dry nitrogen.

Analytical Techniques. ${}^{31}P$ NMR (${}^1H$ decoupled) spectra were obtained with a JEOL FX90Q NMR spectrometer operating at 36.2 MHz. ${}^{31}P$ NMR chemical shifts are relative to 85% H_3PO_4 at 0 ppm with positive shift values downfield from the reference. ${}^1H$ NMR spectra were recorded with the use of a Bruker WP-200 spectrometer operating at 200 MHz. Chemical shifts are relative to tetramethylsilane at δ 0. ${}^{13}C$ NMR (${}^1H$ decoupled) spectra were recorded with the use of a JEOL FX90Q spectrometer operating at 22.5 MHz. All ${}^{13}C$ spectra are referenced to internal tetramethylsilane at 0 ppm. Infrared spectra were obtained with the use of a Perkin-Elmer 283B grating spectrometer. X-ray crystallographic data were collected on an Enraf-Nonius CAD4 diffractometer controlled by a PDP 11/44 computer. The structures were solved by SDP[21] installed on the PDP 11/44. Elemental analyses were obtained by Galbraith Laboratories, Knoxville, TN.

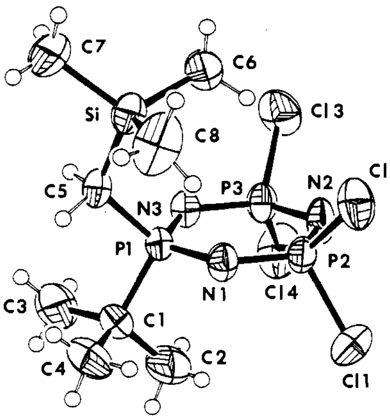


Figure 1. Molecular structure of **1d**.

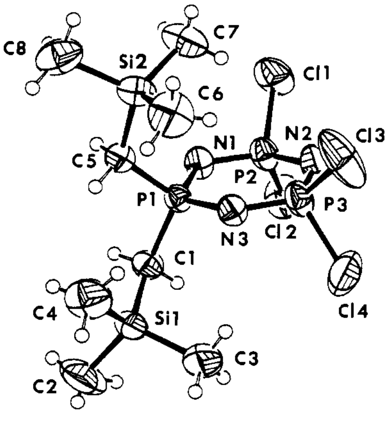


Figure 2. Molecular structure of **7**.

Synthesis of *gem*-$N_3P_3Cl_4(CH_2SiMe_3)(R)$ (1) [R = C_2H_5 (1a), *i*-C_3H_7 (1b), *n*-C_4H_9 (1c), C_6H_5 (1f)].[22] ((Trimethylsilyl)methyl)magnesium chloride, Me_3SiCH_2MgCl, was prepared by the addition of (chloromethyl)trimethylsilane (12.3 g, 0.100 mol) to magnesium (3.65 g, 0.150 mol) in dry THF (200 mL), as described previously.[5] The Grignard solution was transferred to an addition funnel under nitrogen and added dropwise to a solution of $(NPCl_2)_3$ (30.0 g, 0.0865 mol) in dry THF (500 mL) at 66 °C. On completion of addition, the reaction mixture was refluxed at 66 °C for 24 h and then allowed to cool to 25 °C. A THF solution of RMgCl (0.100 mol) (R = C_2H_5, *i*-C_3H_7, *n*-C_4H_9, C_6H_5) was added dropwise over 1 h, and the solution was stirred at 25 °C for 24 h. Solvent was removed under reduced pressure, and diethyl ether (500 mL) was added to the residue. This mixture was washed with 3 × 250 mL portions of 5% HCl (chilled to 0 °C), and the ether layer was dried over $MgSO_4$. Suction filtration through fuller's earth yielded a clear filtrate from which the ether was removed under reduced pressure to yield *gem*-$N_3P_3Cl_4(CH_2SiMe_3)(R)$ as a white solid. Recrystallization from hexane (twice) followed by two sublimations at approximately 100 °C/0.05 mmHg gave pure **1**. (See Tables I–III for complete characterization data.)

Synthesis of *gem*-$N_3P_3Cl_4(CH_2SiMe_3)$(*t*-C_4H_9) (1d) and *gem*-$N_3P_3Cl_4(CH_2SiMe_3)$(*neo*-C_5H_{11}) (1e). Neopentylmagnesium chloride was prepared from neopentyl chloride (42.8 g, 0.400 mol) and magnesium (14.4 g, 0.59 mol) in dry THF (150 mL), as described previously.[6]

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(21) Structure Determination Package (SDP), B. A. Frenz and Associates, Inc., College Station, Texas 77840, and Enraf-Nonius, Delft, Holland, 1982.

(22) In these reactions the organosilyl Grignard reagent was added first to reduce the possibility that bicyclophosphazenes would be formed, a reaction known to occur when $(NPCl_2)_3$ reacts with some non-silyl Grignard reagents.[26]

Table I. Cyclotriphosphazene Characterization Data

R	mp, °C	% yield	mass spectral data, *m/e* found	mass spectral data, *m/e* calcd	elemental anal.	elemental anal. % found	elemental anal. % calcd
gem-$N_3P_3Cl_4(CH_2SiMe_3)(R)$[a]							
C_2H_5 (**1a**)	143–144	76	393[b]	393	C	18.45	18.33
					H	3.73	4.11
					N	10.32	10.69
i-C_3H_7 (**1b**)	86–87	35	407[b]	107	C	20.51	20.65
					H	4.78	4.47
					N	10.41	10.32
n-C_4H_9 (**1c**)	84–85	45	421[b]	421	C	22.91	22.82
					H	4.81	4.80
					N	10.00	9.98
t-C_4H_9 (**1d**)	113–114	25	421[b]	421	C	23.07	22.82
					H	4.80	4.80
					N	10.19	9.98
neo-C_5H_{11} (**1e**)	93–94	23	435[b]	435	C	24.92	24.84
					H	5.07	5.11
					N	9.73	9.66
C_6H_5 (**1f**)	102–103	50	441[b]	441	C	27.11	27.23
					H	3.45	3.66
					N	9.50	9.53
gem-$N_3P_3(OCH_2CF_3)_4(CH_2SiMe_3)(R)$[a]							
C_2H_5 (**2a**)	oil	85	647	647	C	26.12	25.97
					H	3.77	3.74
					N	6.50	6.49
i-C_3H_7 (**2b**)	38–39	76	661	661	C	27.20	27.24
					H	3.66	3.97
					N	6.33	6.35
n-C_4H_9 (**2c**)	oil	71	675	675	C	28.64	28.45
					H	4.18	4.19
					N	6.08	6.22
t-C_4H_9 (**2d**)	65–66	70	675	675	C	28.34	28.45
					H	4.03	4.19
					N	6.31	6.22
neo-C_5H_{11} (**2e**)	oil	71	689	689	C	29.77	29.61
					H	4.53	4.39
					N	6.06	6.10
C_6H_5 (**2f**)	oil	70	695	695	C	31.39	31.08
					H	3.50	3.49
					N	6.06	6.04
gem-$N_3P_3(OCH_2CF_3)_4(CH_3)(R)$[a]							
C_2H_5 (**3a**)	oil	40	575	575	C	23.21	22.97
					H	2.95	2.81
					N	7.11	7.31
i-C_3H_7 (**3b**)	oil	40	589	589	C	24.48	24.46
					H	3.12	3.09
					N	7.11	7.13
n-C_4H_9 (**3c**)	34–35	79	603	603	C	26.07	25.88
					H	3.35	3.35
					N	6.86	6.97
t-C_4H_9 (**3d**)	oil	70	603	603	C	26.07	25.88
					H	3.59	3.35
					N	7.05	6.97
neo-C_5H_{11} (**3e**)	oil	70	617	617	C	27.34	27.24
					H	3.68	3.60
					N	6.54	6.81
C_6H_5 (**3f**)	oil	67	623	623	C	29.00	28.90
					H	2.58	2.59
					N	6.67	6.74

[a] Infrared spectroscopic analysis of compounds **1–3** detected characteristic vibrations for P–N (1250–1150 cm^{-1}), P–O (970 cm^{-1}), P–Cl (600–580, 520–500 cm^{-1}), Si–CH_3 (1260–1250, 850–800 cm^{-1}), C–H (aliphatic, 3000–2900 cm^{-1}), and C–H (aromatic, 3100–3000 cm^{-1}) where applicable. [b] Cl_4 isotope pattern detected.

Table II. Cyclotriphosphazene ^{31}P NMR Data[a]

R (no.)	signal	chem shift, ppm	coupling const, J_{PNP}, Hz
gem-$N_3P_3Cl_4(CH_2SiMe_3)(R)$			
C_2H_5 (**1a**)	$P(Cl)_2$	17.3	unres[b]
	$P(C)_2$	44.7	
i-C_3H_7 (**1b**)	$P(Cl)_2$	17.0	unres
	$P(C)_2$	49.5	
n-C_4H_9 (**1c**)	$P(Cl)_2$	17.0	unres
	$P(C)_2$	42.9	
t-C_4H_9 (**1d**)	$P(Cl)_2$	16.7	unres
	$P(C)_2$	53.8	
neo-C_5H_{11} (**1e**)	$P(Cl)_2$	15.6	unres
	$P(C)_2$	38.4	
C_6H_5 (**1f**)	$P(Cl)_2$	17.1	7.5
	$P(C)_2$	31.5	
gem-$N_3P_3(OCH_2CF_3)_4(CH_2SiMe_3)(R)$			
C_2H_5 (**2a**)	$P(O)_2$	14.8	26.7
	$P(C)_2$	44.9	
i-C_3H_7 (**2b**)	$P(O)_2$	14.6	25.1
	$P(C)_2$	49.3	
n-C_4H_9 (**2c**)	$P(O)_2$	14.7	26.7
	$P(C)_2$	43.6	
t-C_4H_9 (**2d**)	$P(O)_2$	11.7	23.4
	$P(C)_2$	50.8	
neo-C_5H_{11} (**2e**)	$P(O)_2$	13.5	27.3
	$P(C)_2$	40.7	
C_6H_5 (**2f**)	$P(O)_2$	14.6	31.3
	$P(C)_2$	33.8	
gem-$N_3P_3(OCH_2CF_3)_4(CH_3)(R)$			
C_2H_5 (**3a**)	$P(O)_2$	15.7	26.4
	$P(C)_2$	42.5	
i-C_3H_7 (**3b**)	$P(O)_2$	15.7	24.4
	$P(C)_2$	46.7	
n-C_4H_9 (**3c**)	$P(O)_2$	15.5	27.3
	$P(C)_2$	41.2	
t-C_4H_9 (**3d**)	$P(O)_2$	15.8	22.8
	$P(C)_2$	50.8	
neo-C_5H_{11} (**3e**)	$P(O)_2$	14.4	27.3
	$P(C)_2$	38.4	
C_6H_5 (**3f**)	$P(O)_2$	15.2	32.9
	$P(C)_2$	31.2	

[a] $CDCl_3$ solution. [b] Unres = unresolved.

Hexachlorocyclotriphosphazene (20.0 g, 0.0576 mol) and $[(n\text{-}Bu)_3PCuI]_4$ (16.0 g, 0.0100 mol) were dissolved in dry THF (600 mL) and cooled to −78 °C. The THF solution of *neo*-$C_5H_{11}MgCl$ or *t*-C_4H_9MgCl (150.0 mL of 2.0 M solution in THF, 0.300 mol) was added dropwise over a period of 1 h. The reaction mixture was then stirred for 16 h as the temperature was allowed to rise to 25 °C. The reaction mixture was then cooled to 0 °C, and Me_3SiCH_2I (69.4 g, 0.324 mol) was added dropwise over a 1-h period. The reaction mixture was refluxed at 66 °C for 18 h. The products, *gem*-$N_3P_3(CH_2SiMe_3)(R)$ (R = *neo*-C_5H_{11}, *t*-C_4H_9), were isolated and purified, as described above, but with the use of toluene instead of diethyl ether as the extraction solvent. Complete characterization data are given in Tables I–III.

Synthesis of *gem*-$N_3P_3Cl_4(CH_3)(R)$ (8) [R = C_2H_5 (8a), *i*-C_3H_7 (8b), *n*-C_4H_9 (8c), *t*-C_4H_9 (8d), *neo*-C_5H_{11} (8e), C_6H_5 (8f)]. These compounds were prepared by synthetic techniques described previously.[6,12,13]

Synthesis of *gem*-$N_3P_3(OCH_2CF_3)_4(CH_2SiMe_3)(R)$ (2) [R = C_2H_5 (2a), *i*-C_3H_7 (2b), *n*-C_4H_9 (2c), *t*-C_4H_9 (2d), *neo*-C_5H_{11} (2e), C_6H_5 (2f)]. Trifluoroethanol (3.30 g, 0.0330 mol) was added dropwise to a slurry of NaH (0.72 g, 0.0300 mol) in dry toluene (150 mL). The reaction mixture was then refluxed at 110 °C for 4 h to ensure complete formation of CF_3CH_2ONa and then cooled to 25 °C. Compound **1** (0.005 mol) was added to the reaction mixture, which was then refluxed at 110 °C for 24 h (in the case of **2d**, a reaction time of 72–96 h was usually required). When cooled, the reaction mixture was poured into 5% aqueous HCl (250 mL) and then extracted with three 100-mL portions of diethyl ether. The ether layer was dried over $MgSO_4$ and filtered through fuller's earth, and the ether was removed under reduced pressure to yield an oil. The oil was vacuum-distilled twice at 90–130 °C/0.05 mmHg to yield pure **2** as an oil or a solid. The compounds where R = *i*-C_3H_7 (**2b**) and *t*-C_4H_9 (**2d**) were recrystallized from hexane to yield white solids. Complete characterization data are given in Tables I–III.

Synthesis of *gem*-$N_3P_3(OCH_2CF_3)_4(CH_3)(R)$ (3) [R = C_2H_5 (3a), *i*-C_3H_7 (3b), *n*-C_4H_9 (3c), *t*-C_4H_9 (3d), *neo*-C_5H_{11} (3e), C_6H_5 (3f)]. A THF solution CF_3CH_2ONa was prepared by the careful dropwise addition of CF_3CH_2OH (5.50 g, 0.0550 mol) to NaH (1.20 g, 0.0500 mol) in dry THF (100 mL). On completion of hydrogen evolution, compound **1** or **8** (0.0050 mol) was added to the CF_3CH_2ONa solution. The reaction mixture was stirred at 25 °C for 1 h, followed by reflux at 66 °C for 24 h (in the case of **3d**, a reaction time of 72–96 h was usually required), and then cooled to 25 °C. The reaction mixture was poured into 5% aqueous HCl (100 mL) and extracted with three 100-mL portions of diethyl ether. The ether layer was dried over $MgSO_4$ and suction-filtered through fuller's earth, and the solvent was then removed

Table III. Cyclotriphosphazene ^{1}H NMR and ^{13}C NMR Data

gem-$N_3P_3Cl_4(CH_2SiMe_3)(R)$

R (no.)	signal	^{1}H NMR, $\delta^{a,b}$	^{13}C NMR, ppm^{a,b}	coupling const, Hz	
				PCH_2SiMe_3	PR
C_2H_5 (**1a**)	$\mathrm{P}\mathit{CH}_2\mathrm{Si(CH_3)_3}$	1.26 (dt), 2 H	19.03 (dt)	$J_{\mathrm{PCH}} = 16.0$	$J_{\mathrm{PCCH}} = 21.2$
	$\mathrm{PCH_2Si(}\mathit{CH}_3\mathrm{)_3}$	0.23 (s), 9 H	0.06 (d)	$J_{\mathrm{PNPCH}} = 3.9$	$J_{\mathrm{HCCH}} = 7.9$
	$\mathrm{P}\mathit{CH}_2\mathrm{CH_3}$	1.83 (m), 2 H	29.00 (dt)	$J_{\mathrm{PC}} = 91.6$	$J_{\mathrm{PC}} = 90.3$
	$\mathrm{PCH_2}\mathit{CH}_3$	1.20 (dt), 3 H	5.70 (d)	$J_{\mathrm{PNPC}} = 5.5$	J_{PNPC} = unres^c
				$J_{\mathrm{PCSiC}} = 3.7$	$J_{\mathrm{PCC}} = 6.1$
i-C_3H_7 (**1b**)	$\mathrm{P}\mathit{CH}_2\mathrm{Si(CH_3)_3}$	1.23 (dt), 2 H	17.87 (dt)	$J_{\mathrm{PCH}} = 15.0$	$J_{\mathrm{PCCH}} = 19.6$
	$\mathrm{PCH_2Si(}\mathit{CH}_3\mathrm{)_3}$	0.25 (s), 9 H	0.15 (d)	$J_{\mathrm{PNPCH}} = 4.2$	$J_{\mathrm{HCCH}} = 6.9$
	$\mathrm{P}\mathit{CH}\mathrm{(CH_3)_2}$	1.89 (m), 1 H	33.68 (dt)	$J_{\mathrm{PC}} = 83.8$	$J_{\mathrm{PC}} = 88.9$
	$\mathrm{PCH(}\mathit{CH}_3\mathrm{)_2}$	1.21 (dd), 6 H	15.55 (s)	$J_{\mathrm{PNPC}} = 5.1$	J_{PNPC} = unres
				$J_{\mathrm{PCSiC}} = 3.4$	
n-C_4H_9 (**1c**)	$\mathrm{P}\mathit{CH}_2\mathrm{Si(CH_3)_3}$	1.25 (dt), 2 H	21.28 (dt)	$J_{\mathrm{PCH}} = 16.2$	$J_{\mathrm{HCCH}} = 7.2$
	$\mathrm{PCH_2Si(}\mathit{CH}_3\mathrm{)_3}$	0.22 (s), 9 H	−0.07 (d)	$J_{\mathrm{PNPCH}} = 3.9$	$J_{\mathrm{PC}} = 89.1$
	$\mathrm{P}\mathit{CH}_2\mathrm{CH_2CH_2CH_3}$		35.53 (dt)	$J_{\mathrm{PC}} = 84.2$	$J_{\mathrm{PNPC}} = 2.1$
	$\mathrm{PCH_2}\mathit{CH}_2\mathrm{CH_2CH_3}$	1.85–1.38 (m), 6 H	23.43 (d)		
	$\mathrm{PCH_2CH_2}\mathit{CH}_2\mathrm{CH_3}$		23.60 (d)	$J_{\mathrm{PNPC}} = 5.2$	$J_{\mathrm{PCC}} = 17.7$
	$\mathrm{PCH_2CH_2CH_2}\mathit{CH}_3$	0.93 (t), 3 H	13.54 (s)	$J_{\mathrm{PCSiC}} = 3.1$	$J_{\mathrm{PCCC}} = 5.5$
t-C_4H_9 (**1d**)	$\mathrm{P}\mathit{CH}_2\mathrm{Si(CH_3)_3}$	1.16 (dt), 2 H	14.03 (dt)	$J_{\mathrm{PCH}} = 13.9$	$J_{\mathrm{PCCH}} = 17.6$
	$\mathrm{PCH_2Si(}\mathit{CH}_3\mathrm{)_3}$	0.23 (s), 9 H	1.10 (d)	$J_{\mathrm{PNPCH}} = 4.7$	$J_{\mathrm{PC}} = 87.2$
	$\mathrm{PC(}\mathit{CH}_3\mathrm{)_3}$	1.17 (d), 9 H	23.75 (s)	$J_{\mathrm{PC}} = 81.8$	J_{PNPC} = unres
	$\mathrm{P}\mathit{C}\mathrm{(CH_3)_3}$		36.40 (dt)	$J_{\mathrm{PNPC}} = 5.1$	
				$J_{\mathrm{PCSiC}} = 4.4$	
neo-C_5H_{11} (**1e**)	$\mathrm{P}\mathit{CH}_2\mathrm{Si(CH_3)_3}$	1.31 (dt), 2 H	24.87 (dt)	$J_{\mathrm{PCH}} = 16.8$	$J_{\mathrm{PCH}} = 12.7$
	$\mathrm{PCH_2Si(}\mathit{CH}_3\mathrm{)_3}$	0.24 (s), 9 H	0.10 (d)	$J_{\mathrm{PNPCH}} = 3.2$	$J_{\mathrm{PNPCH}} = 2.6$
	$\mathrm{P}\mathit{CH}_2\mathrm{C(CH_3)_3}$	1.88 (dt), 2 H	48.94 (dt)	$J_{\mathrm{PC}} = 82.4$	$J_{\mathrm{PC}} = 87.9$
	$\mathrm{PCH_2C(}\mathit{CH}_3\mathrm{)_3}$	1.17 (s), 9 H	31.08 (d)	$J_{\mathrm{PNPC}} = 4.3$	J_{PNPC} = unres
				$J_{\mathrm{PCSiC}} = 3.7$	$J_{\mathrm{PCCC}} = 7.9$
C_6H_5 (**1f**)	$\mathrm{P}\mathit{CH}_2\mathrm{Si(CH_3)_3}$	1.23 (dt), 2 H	23.90 (dt)	$J_{\mathrm{PCH}} = 17.4$	$J_{\mathrm{PC}} = 125.2$
	$\mathrm{PCH_2Si(}\mathit{CH}_3\mathrm{)_3}$	−0.05 (s), 9 H	−0.15 (d)	$J_{\mathrm{PNPCH}} = 8.8$	$J_{\mathrm{PCC}} = 13.7$
	$\mathrm{P}\mathit{C}_6\mathit{H}_6$				
	ipso		135.56 (d)	$J_{\mathrm{PC}} = 88.9$	$J_{\mathrm{PCCC}} = 10.3$
	ortho	7.58 (m), 2 H	128.66 (d)		
	meta	7.27 (m), 2 H	129.50 (d)	$J_{\mathrm{PNPC}} = 6.0$	$J_{\mathrm{PCCCC}} = 3.0$
	para	7.27 (m), 1 H	132.02 (d)	$J_{\mathrm{PCSiC}} = 3.4$	

gem-$N_3P_3(OCH_2CF_3)_4(CH_2SiMe_3)(R)$

R (no.)	signal	^{1}H NMR, $\delta^{a,b}$	^{13}C NMR, ppm^{a,b}	coupling const, Hz	
				PCH_2SiMe_3	PR
C_2H_5 (**2a**)	$\mathrm{P}\mathit{CH}_2\mathrm{Si(CH_3)_3}$	1.08 (dt), 2 H	21.62 (dt)	$J_{\mathrm{PCH}} = 20.0$	$J_{\mathrm{PCCH}} = 17.2$
	$\mathrm{PCH_2Si(}\mathit{CH}_3\mathrm{)_3}$	0.15 (s), 9 H	−0.30 (d)	$J_{\mathrm{PNPCH}} = 7.5$	J_{HCCH} = unres
	$\mathrm{P}\mathit{CH}_2\mathrm{CH_3}$	1.70 (m), 2 H	28.94 (d)	$J_{\mathrm{PC}} = 85.5$	$J_{\mathrm{PC}} = 94.0$
	$\mathrm{PCH_2}\mathit{CH}_3$	1.17 (dt), 3 H	5.43 (d)	$J_{\mathrm{PNPC}} = 4.3$	$J_{\mathrm{PCC}} = 5.1$
	$\mathrm{PO}\mathit{CH}_2\mathrm{CF_3}$	4.22 (m), 8 H	62.52 (q)	$J_{\mathrm{PCSiC}} = 3.4$	
	$\mathrm{POCH_2}\mathit{CF}_3$		122.75 (qt)		
i-C_3H_7 (**2b**)	$\mathrm{P}\mathit{CH}_2\mathrm{Si(CH_3)_3}$	1.17 (dt), 2 H	18.25 (dt)	$J_{\mathrm{PCH}} = 16.1$	$J_{\mathrm{PCCH}} = 18.6$
	$\mathrm{PCH_2Si(}\mathit{CH}_3\mathrm{)_3}$	0.17 (s), 9 H	−0.15 (d)	$J_{\mathrm{PNPCH}} = 2.9$	$J_{\mathrm{HCCH}} = 7.0$
	$\mathrm{P}\mathit{CH}\mathrm{(CH_3)_2}$	1.76 (m), 1 H	33.15 (d)	$J_{\mathrm{PC}} = 83.8$	$J_{\mathrm{PC}} = 92.3$
	$\mathrm{PCH(}\mathit{CH}_3\mathrm{)_2}$	1.12 (dd), 6 H	15.17 (d)	$J_{\mathrm{PNPC}} = 4.3$	$J_{\mathrm{PCC}} = 3.4$
	$\mathrm{PO}\mathit{CH}_2\mathrm{CF_3}$	4.23 (m), 8 H	62.54 (q)	$J_{\mathrm{PCSiC}} = 3.4$	
	$\mathrm{POCH_2}\mathit{CF}_3$		122.78 (qt)		
n-C_4H_9 (**2c**)	$\mathrm{P}\mathit{CH}_2\mathrm{Si(CH_3)_3}$	1.20 (dt), 2 H	22.14 (dt)	$J_{\mathrm{PCH}} = 17.4$	$J_{\mathrm{HCCH}} = 7.0$
	$\mathrm{PCH_2Si(}\mathit{CH}_3\mathrm{)_3}$	0.18 (s), 9 H	−0.15 (d)	$J_{\mathrm{PNPCH}} = 2.5$	$J_{\mathrm{PC}} = 92.2$
	$\mathrm{P}\mathit{CH}_2\mathrm{CH_2CH_2CH_3}$		35.87 (dt)	$J_{\mathrm{PC}} = 84.8$	$J_{\mathrm{PCC}} = 17.7$
	$\mathrm{PCH_2}\mathit{CH}_2\mathrm{CH_2CH_3}$	1.75–1.38 (m), 6 H	23.68 (d)		
	$\mathrm{PCH_2CH_2}\mathit{CH}_2\mathrm{CH_3}$		23.80 (d)	$J_{\mathrm{PNPC}} = 4.6$	$J_{\mathrm{PCCC}} = 4.9$
	$\mathrm{PCH_2CH_2CH_2}\mathit{CH}_3$	0.42 (t), 3 H	13.46 (s)	$J_{\mathrm{PCSiC}} = 3.1$	
	$\mathrm{PO}\mathit{CH}_2\mathrm{CF_3}$	4.24 (m), 8 H	62.55 (qt)		
	$\mathrm{POCH_2}\mathit{CF}_3$		122.79 (qt)		
t-C_4H_9 (**2d**)	$\mathrm{P}\mathit{CH}_2\mathrm{Si(CH_3)_3}$	1.15 (dt), 2 H	14.70 (dt)	$J_{\mathrm{PCH}} = 14.6$	$J_{\mathrm{PCCH}} = 16.8$
	$\mathrm{PCH_2Si(}\mathit{CH}_3\mathrm{)_3}$	0.18 (s), 9 H	−0.21 (d)	$J_{\mathrm{PNPCH}} = 3.0$	$J_{\mathrm{PC}} = 91.6$
	$\mathrm{P}\mathit{C}\mathrm{(CH_3)_3}$		35.12 (d)	$J_{\mathrm{PC}} = 85.4$	
	$\mathrm{PC(}\mathit{CH}_3\mathrm{)_3}$	1.11 (d), 9 H	23.56 (s)	$J_{\mathrm{PNPC}} = 5.5$	
	$\mathrm{PO}\mathit{CH}_2\mathrm{CF_3}$	4.25 (m), 8 H	62.62 (q)	$J_{\mathrm{PCSiC}} = 3.1$	
	$\mathrm{POCH_2}\mathit{CF}_3$		122.78 (qt)		
neo-C_5H_{11} (**2e**)	$\mathrm{P}\mathit{CH}_2\mathrm{Si(CH_3)_3}$	1.20 (dt), 2 H	25.82 (dt)	$J_{\mathrm{PCH}} = 17.7$	$J_{\mathrm{PCH}} = 13.0$
	$\mathrm{PCH_2Si(}\mathit{CH}_3\mathrm{)_3}$	0.16 (s), 9 H	0.04 (d)	$J_{\mathrm{PNPCH}} = 2.0$	$J_{\mathrm{PNPCH}} = 2.0$
	$\mathrm{P}\mathit{CH}_2\mathrm{C(CH_3)_3}$	1.76 (dt), 2 H	48.87 (dt)	$J_{\mathrm{PC}} = 83.6$	$J_{\mathrm{PC}} = 90.9$
	$\mathrm{PCH_2C(}\mathit{CH}_3\mathrm{)_3}$	1.10 (s), 9 H	31.02 (d)	$J_{\mathrm{PNPC}} = 4.0$	$J_{\mathrm{PNPC}} = 3.4$
	$\mathrm{PO}\mathit{CH}_2\mathrm{CF_3}$	4.22 (m), 8 H	62.52 (q)	$J_{\mathrm{PCSiC}} = 3.1$	$J_{\mathrm{PCCC}} = 7.9$
	$\mathrm{POCH_2}\mathit{CF}_3$		122.78 (qt)		
C_6H_5 (**2f**)	$\mathrm{P}\mathit{CH}_2\mathrm{Si(CH_3)_3}$	1.44 (dt), 2 H	24.60 (dt)	$J_{\mathrm{PCH}} = 18.6$	$J_{\mathrm{PC}} = 125.7$
	$\mathrm{PCH_2Si(}\mathit{CH}_3\mathrm{)_3}$	0.06 (s), 9 H	−0.36 (d)	$J_{\mathrm{PNPCH}} = 2.8$	$J_{\mathrm{PNPC}} = 2.4$

Table III (Continued)

R (no.)	signal	^{1}H NMR, $\delta^{a,b}$	^{13}C NMR, ppm^{a,b}	coupling const, Hz PCH_2SiMe_3	 PR
C_6H_5 (**2f**)	$\mathrm{P}\mathit{C_6H_5}$				
	ipso		137.51 (dt)	$J_{PC} = 90.9$	$J_{PCC} = 12.8$
	ortho	7.79 (m), 2 H	128.53 (d)		
	meta	7.49 (m), 2 H	129.26 (d)	$J_{PNPC} = 5.8$	$J_{PCCC} = 10.4$
	para	7.49 (m), 1 H	131.57 (d)		
				$J_{PCSiC} = 3.7$	$J_{PCCCC} = 3.1$
	$\mathrm{PO}\mathit{CH}_2\mathrm{CF}_3$	4.32 (m), 4 H	62.75 (qdt)		
		4.02 (m), 4 H	62.27 (qdt)		
	$\mathrm{POCH_2}\mathit{CF}_3$		122.63 (qt)		
			122.41 (qt)		

gem-$N_3P_3(OCH_2CF_3)_4(CH_3)(R)$

R (no.)	signal	^{1}H NMR, $\delta^{a,b}$	^{13}C NMR, ppm^{a,b}	coupling const, Hz PCH_3	 PR
C_2H_5 (**3a**)	$\mathrm{P}\mathit{CH}_3$	1.53 (dt), 3 H	18.98 (dt)	$J_{PCH} = 13.8$	$J_{PCCH} = 20.3$
	$\mathrm{P}\mathit{CH}_2\mathrm{CH}_3$	1.76 (m), 2 H	26.83 (dt)	$J_{PNPCH} = 1.7$	$J_{HCCH} = 7.5$
	$\mathrm{PCH_2}\mathit{CH}_3$	1.14 (dt), 3 H	5.11 (d)	$J_{PC} = 94.0$	$J_{PC} = 94.6$
	$\mathrm{PO}\mathit{CH}_2\mathrm{CF}_3$	4.25 (m), 8 H	62.61 (q)	$J_{PNPC} = 3.7$	$J_{PNPC} = 3.4$
	$\mathrm{POCH_2}\mathit{CF}_3$		122.75 (qt)		$J_{PCC} = 6.1$
i-C_3H_7 (**3b**)	$\mathrm{P}\mathit{CH}_3$	1.50 (dt), 3 H	16.79 (dt)	$J_{PCH} = 13.4$	$J_{PCCH} = 18.8$
	$\mathrm{P}\mathit{CH}\mathrm{(CH_3)_2}$	1.82 (m), 1 H	31.23 (dt)	$J_{PNPCH} = 3.4$	$J_{HCCH} = 7.0$
	$\mathrm{PCH(}\mathit{CH}_3\mathrm{)_2}$	1.14 (dd), 6 H	14.79 (d)	$J_{PC} = 92.8$	$J_{PC} = 94.0$
	$\mathrm{PO}\mathit{CH}_2\mathrm{CF}_3$	4.24 (m), 8 H	62.59 (q)	J_{PNPC} = unres	$J_{PNPC} = 3.1$
	$\mathrm{POCH_2}\mathit{CF}_3$		122.75 (qt)		$J_{PCC} = 1.2$
n-C_4H_9 (**3c**)	$\mathrm{P}\mathit{CH}_3$	1.52 (dt), 3 H	19.60 (dt)	$J_{PCH} = 13.9$	$J_{HCCH} = 7.0$
	$\mathrm{P}\mathit{CH}_2\mathrm{CH_2CH_2CH_3}$		33.57 (dt)	$J_{PNPCH} = 1.7$	$J_{PC} = 93.4$
	$\mathrm{PCH_2}\mathit{CH}_2\mathrm{CH_2CH_3}$	1.80–1.35 (m), 6 H	23.58 (d)		
	$\mathrm{PCH_2CH_2}\mathit{CH}_2\mathrm{CH_3}$		23.39 (d)	$J_{PC} = 94.0$	$J_{PNPC} = 3.4$
	$\mathrm{PCH_2CH_2CH_2}\mathit{CH}_3$	0.92 (t), 3 H	13.40 (s)	$J_{PNPC} = 3.7$	$J_{PCC} = 17.1$
	$\mathrm{PO}\mathit{CH}_2\mathrm{CF}_3$	4.24 (m), 8 H	62.59 (q)		$J_{PCCC} = 4.9$
	$\mathrm{POCH_2}\mathit{CF}_3$		122.74 (qt)		
t-C_4H_9 (**3d**)	$\mathrm{P}\mathit{CH}_3$	1.47 (dt), 3 H	14.67 (dt)	$J_{PCH} = 13.1$	$J_{PCCH} = 17.0$
	$\mathrm{P}\mathit{C}\mathrm{(CH_3)_3}$		33.24 (dt)	$J_{PNPCH} = 1.7$	$J_{PC} = 93.4$
	$\mathrm{PC(}\mathit{CH}_3\mathrm{)_3}$	1.11 (d), 9 H	23.29 (s)	$J_{PC} = 90.3$	$J_{PNPC} = 3.1$
	$\mathrm{PO}\mathit{CH}_2\mathrm{CF}_3$	4.22 (m), 8 H	62.58 (q)	$J_{PNPC} = 4.0$	
	$\mathrm{POCH_2}\mathit{CF}_3$		122.80 (qt)		
neo-C_5H_{11} (**3e**)	$\mathrm{P}\mathit{CH}_3$	1.52 (dt), 3 H	22.97 (dt)	$J_{PCH} = 13.7$	$J_{PCH} = 13.5$
	$\mathrm{P}\mathit{CH}_2\mathrm{C(CH_3)_3}$	1.78 (dt), 2 H	47.15 (dt)	J_{PNPCH} = unres	J_{PNPCH} = unres
	$\mathrm{PCH_2C(}\mathit{CH}_3\mathrm{)_3}$	1.10 (s), 9 H	30.94 (d)	$J_{PC} = 93.4$	$J_{PC} = 92.2$
	$\mathrm{PO}\mathit{CH}_2\mathrm{CF}_3$	4.21 (m), 8 H	62.64 (q)	$J_{PNPC} = 3.1$	$J_{PNPC} = 4.0$
	$\mathrm{POCH_2}\mathit{CF}_3$		122.78 (qt)		$J_{PCCC} = 7.9$
C_6H_5 (**3f**)	$\mathrm{P}\mathit{CH}_3$	1.74 (dt), 3 H	21.99 (dt)	$J_{PCH} = 14.6$	$J_{PC} = 125.7$
	$\mathrm{P}\mathit{C_6H_5}$				
	ipso		135.08 (dt)	$J_{PNPCH} = 2.0$	$J_{PNPC} = 3.0$
	ortho	7.81 (m), 2 H	128.68 (d)		
	meta	7.53 (m), 2 H	129.33 (d)	$J_{PC} = 101.3$	$J_{PCC} = 13.4$
	para	7.53 (m), 1 H	132.00 (d)		
				$J_{PNPC} = 5.2$	$J_{PCCC} = 11.0$
	$\mathrm{PO}\mathit{CH}_2\mathrm{CF}_3$	4.33 (m), 4 H	62.75 (qt)		
					$J_{PCCCC} = 3.0$
		4.10 (m), 4 H	62.47 (qt)		
	$\mathrm{POCH_2}\mathit{CF}_3$		122.59 (qm)		

[a] $CDCl_3$ solution. [b] Key: singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m). [c] Unres = unresolved.

Table IV. Bond Lengths (Å) for *gem*-$N_3P_3Cl_4(CH_2SiMe_3)(t\text{-}C_4H_9)$ (**1d**)

Cl(1)–P(2)	2.002 (1)	P(3)–N(2)	1.579 (2)
Cl(2)–P(2)	2.003 (1)	P(3)–N(3)	1.551 (1)
Cl(3)–P(3)	2.005 (1)	Si–C(5)	1.894 (2)
Cl(4)–P(3)	1.997 (1)	Si–C(6)	1.850 (2)
P(1)–N(1)	1.620 (1)	Si–C(7)	1.853 (2)
P(1)–N(3)	1.619 (1)	Si–C(8)	1.855 (3)
P(1)–C(1)	1.813 (2)	C(1)–C(2)	1.520 (4)
P(1)–C(5)	1.776 (2)	C(1)–C(3)	1.533 (3)
P(2)–N(1)	1.550 (1)	C(1)–C(4)	1.540 (4)
P(2)–N(2)	1.570 (2)		

Table V. Bond Lengths (Å) for *gem*-$N_3P_3Cl_4(CH_2SiMe_3)_2$ (**7**)

Cl(1)–P(2)	2.005 (1)	P(3)–N(2)	1.585 (2)
Cl(2)–P(2)	2.018 (1)	P(3)–N(3)	1.550 (2)
Cl(3)–P(3)	1.987 (1)	Si(1)–C(1)	1.903 (2)
Cl(4)–P(3)	2.010 (1)	Si(1)–C(2)	1.867 (3)
P(1)–N(1)	1.635 (1)	Si(1)–C(3)	1.850 (3)
P(1)–N(3)	1.623 (2)	Si(1)–C(4)	1.858 (3)
P(1)–C(1)	1.786 (2)	Si(2)–C(5)	1.884 (2)
P(1)–C(5)	1.775 (2)	Si(2)–C(6)	1.857 (3)
P(2)–N(1)	1.554 (2)	Si(2)–C(7)	1.847 (3)
P(2)–N(2)	1.577 (2)	Si(2)–C(8)	1.871 (3)

from the filtrate to yield an oil. The oil was vacuum-distilled twice at 90–130 °C/0.05 mmHg to yield pure **3** as a clear oil. The compound where R = *n*-C_4H_9 (**3c**) was recrystallized from hexane to yield a white solid. Complete characterization data are given in Tables I–III.

X-ray Structure Determination Technique. Our general X-ray structure determination technique has been described previously,[13,23,24] and only the details related to the present work will be given here. Crystals of **1d** and **7** were grown from hexane/CH_2Cl_2 solution by slow evapo-

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Table VI. Bond Angles (deg) for *gem*-$N_3P_3Cl_4(CH_2SiMe_3)(t\text{-}C_4H_9)$ (**1d**)

N(1)–P(1)–N(3)	113.94 (7)	N(2)–P(3)–N(3)	119.65 (8)
N(1)–P(1)–C(1)	107.57 (9)	C(5)–Si–C(6)	111.3 (1)
N(1)–P(1)–C(5)	109.78 (9)	C(5)–Si–C(7)	104.8 (1)
N(3)–P(1)–C(1)	108.67 (9)	C(5)–Si–C(8)	110.1 (2)
N(3)–P(1)–C(5)	107.93 (9)	C(6)–Si–C(7)	110.9 (1)
C(1)–P(1)–C(5)	108.85 (9)	C(6)–Si–C(8)	109.8 (2)
Cl(1)–P(2)–Cl(2)	99.56 (3)	C(7)–Si–C(8)	109.8 (2)
Cl(1)–P(2)–N(1)	111.18 (6)	P(1)–N(1)–P(2)	123.15 (9)
Cl(1)–P(2)–N(2)	107.93 (7)	P(2)–N(2)–P(3)	119.98 (9)
Cl(2)–P(2)–N(1)	109.50 (6)	P(1)–N(3)–P(3)	122.74 (9)
Cl(2)–P(2)–N(2)	107.19 (7)	P(1)–C(1)–C(2)	108.3 (2)
N(1)–P(2)–N(2)	119.56 (8)	P(1)–C(1)–C(3)	109.9 (2)
Cl(3)–P(3)–Cl(4)	99.62 (4)	P(1)–C(1)–C(4)	108.9 (2)
Cl(3)–P(3)–N(2)	107.27 (7)	C(2)–C(1)–C(3)	110.4 (3)
Cl(3)–P(3)–N(3)	109.55 (6)	C(2)–C(1)–C(4)	109.3 (3)
Cl(4)–P(3)–N(2)	108.32 (7)	C(3)–C(1)–C(4)	110.1 (3)
Cl(4)–P(3)–N(3)	110.53 (6)	P(1)–C(5)–Si	119.3 (1)

Table VII. Bond Angles (deg) for *gem*-$N_3P_3Cl_4(CH_2SiMe_3)_2$ (**7**)

N(1)–P(1)–N(3)	113.09 (8)	C(1)–Si(1)–C(2)	105.4 (2)
N(1)–P(1)–C(1)	109.49 (9)	C(1)–Si(1)–C(3)	109.7 (2)
N(1)–P(1)–C(5)	107.04 (9)	C(1)–Si(1)–C(4)	112.1 (1)
N(3)–P(1)–C(1)	109.15 (9)	C(2)–Si(1)–C(3)	110.6 (2)
N(3)–P(1)–C(5)	110.02 (9)	C(2)–Si(1)–C(4)	109.3 (2)
C(1)–P(1)–C(5)	107.9 (1)	C(3)–Si(1)–C(4)	109.8 (3)
Cl(1)–P(2)–Cl(2)	99.89 (4)	C(5)–Si(2)–C(6)	109.8 (2)
Cl(1)–P(2)–N(1)	108.98 (7)	C(5)–Si(2)–C(7)	110.0 (1)
Cl(1)–P(2)–N(2)	107.38 (8)	C(5)–Si(2)–C(8)	104.9 (1)
Cl(2)–P(2)–N(1)	110.39 (7)	C(6)–Si(2)–C(7)	112.9 (2)
Cl(2)–P(2)–N(2)	107.97 (9)	C(6)–Si(2)–C(8)	108.0 (2)
N(1)–P(2)–N(2)	120.28 (9)	C(7)–Si(2)–C(8)	111.0 (2)
Cl(3)–P(3)–Cl(4)	100.32 (6)	P(1)–N(1)–P(2)	122.4 (1)
Cl(3)–P(3)–N(2)	107.29 (8)	P(2)–N(2)–P(3)	118.5 (1)
Cl(3)–P(3)–N(3)	109.90 (7)	P(1)–N(3)–P(3)	123.2 (1)
Cl(4)–P(3)–N(2)	107.32 (9)	P(1)–C(1)–Si(1)	120.2 (1)
Cl(4)–P(3)–N(3)	110.11 (7)	P(1)–C(5)–Si(2)	121.4 (1)
N(2)–P(3)–N(3)	120.07 (9)		

Table VIII. Positional Parameters and Their Estimated Standard Deviations for *gem*-$N_3P_3Cl_4(CH_2SiMe_3)(t\text{-}C_4H_9)$ (**1d**)

atom	*x*	*y*	*z*
Cl(1)	0.29345 (8)	0.23396 (6)	0.23054 (5)
Cl(2)	0.17189 (6)	0.26193 (5)	0.37650 (6)
Cl(3)	0.45146 (6)	0.24934 (6)	0.54846 (6)
Cl(4)	0.55822 (7)	0.22507 (6)	0.39294 (8)
P(1)	0.39220 (5)	0.43727 (4)	0.36855 (4)
P(2)	0.29651 (5)	0.28897 (4)	0.33902 (5)
P(3)	0.44723 (5)	0.28291 (5)	0.43213 (5)
Si	0.25332 (6)	0.50863 (5)	0.49602 (6)
N(1)	0.3075 (2)	0.3861 (1)	0.3316 (1)
N(2)	0.3632 (2)	0.2375 (1)	0.3934 (2)
N(3)	0.4571 (1)	0.3803 (1)	0.4249 (1)
C(1)	0.4574 (2)	0.4776 (2)	0.2848 (2)
C(2)	0.4930 (3)	0.4028 (3)	0.2370 (2)
C(3)	0.5355 (3)	0.5316 (3)	0.3162 (3)
C(4)	0.3958 (3)	0.5312 (2)	0.2306 (2)
C(5)	0.3533 (2)	0.5239 (2)	0.4270 (2)
C(6)	0.2628 (2)	0.4090 (2)	0.5538 (2)
C(7)	0.2554 (3)	0.6014 (2)	0.5641 (2)
C(8)	0.1477 (2)	0.5086 (2)	0.4367 (3)

Table IX. Positional Parameters and Their Estimated Standard Deviations for *gem*-$N_3P_3Cl_4(CH_2SiMe_3)_2$ (**7**)

atom	*x*	*y*	*z*
Cl(1)	0.25942 (8)	0.30041 (8)	0.01147 (4)
Cl(2)	0.12096 (8)	0.11873 (9)	−0.09959 (6)
Cl(3)	0.46356 (11)	0.47680 (8)	−0.18300 (6)
Cl(4)	0.29661 (11)	0.27849 (13)	−0.27172 (5)
P(1)	0.53151 (6)	0.11833 (5)	−0.09534 (3)
P(2)	0.29271 (7)	0.21703 (6)	−0.07207 (4)
P(3)	0.39795 (8)	0.30963 (7)	−0.17418 (4)
Si(1)	0.60934 (8)	−0.06185 (7)	−0.20513 (4)
Si(2)	0.77007 (8)	0.27364 (7)	−0.00172 (4)
N(1)	0.4177 (2)	0.1325 (2)	−0.0500 (1)
N(2)	0.2893 (2)	0.3167 (2)	−0.1288 (1)
N(3)	0.5202 (2)	0.2221 (2)	−0.1538 (1)
C(1)	0.5152 (2)	−0.0268 (2)	−0.1356 (1)
C(2)	0.6003 (5)	−0.2296 (3)	−0.2157 (2)
C(3)	0.5240 (5)	0.0140 (4)	−0.2862 (2)
C(4)	0.7899 (3)	−0.0144 (4)	−0.1799 (2)
C(5)	0.6928 (2)	0.1251 (2)	−0.0370 (1)
C(6)	0.8229 (4)	0.3601 (3)	−0.0706 (2)
C(7)	0.6503 (3)	0.3580 (3)	0.0375 (2)
C(8)	0.9265 (3)	0.2315 (4)	0.0645 (2)

Table X. Summary of Crystal Data and Collection Parameters

	1d	**7**
formula	$C_8H_{20}Cl_4N_3P_3Si$	$C_8H_{22}Cl_4N_3P_3Si_2$
fw	421.1	451.2
cryst size, mm	0.40 × 0.32 × 0.21	0.63 × 0.45 × 0.54
space group	*Pbca*	$P2_1/n$
a, Å	14.884 (4)	10.145 (4)
b, Å	15.815 (4)	11.060 (5)
c, Å	16.615 (4)	19.999 (6)
β, deg		103.56 (3)
V, Å^3	3910.9	2181.4
Z	8	4
D(calcd), g/cm^3	1.43	1.37
radiation	Mo Kα	Mo Kα
θ limits, deg	25	25
μ, cm^{-1}	9.03	8.7
λ, Å	0.71073	0.71073
T, K	293	293
scan method	$\omega/2\theta$	$\omega/2\theta$
ω-scan width, deg	0.80 + 0.35 tan θ	0.60 + 0.35 tan θ
cryst decay	3.3%	2.0%
empirical abs cor		
min cor factor	0.961	0.965
max cor factor	1.000	1.000
no. of unique data measd	3445	3827
no. of data used $[I > 3\sigma(I)]$	2723	3179
data:param ratio	11.0	8.4
R, R_w $(=(\sum\Delta^2/\sum wF_o^2)^{1/2})$	0.0365, 0.0461	0.042, 0.061
$(\Delta/\sigma)_{max}$ in last cycle	0.15	0.30
$\Delta\rho$ in final ΔF map, e Å^{-3}	0.26	0.48
final *p* param in weighting scheme	0.020	0.050
av shift/error	2.81	2.068

ration of the solvent. A summary of the important crystallographic data is presented in Table X.

The structures were solved by direct methods using MULTAN 82.[25] In each case, the first *E* map revealed the positions of all non-hydrogen atoms. Both structures were refined by full-matrix, least-squares calculations with anisotropic thermal parameters for the non-hydrogen atoms. Difference Fourier syntheses, calculated toward the end of refinement, showed maxima consistent with the expected positions of H atoms in both structures. The H atoms were included in the refinement at their idealized geometric positions (C–H = 0.95 Å). At the conclusion of the refinements, the values of *R* and R_w were 0.0365 and 0.0461, respectively, for **1d** and 0.042 and 0.061, respectively, for **7**. In the refinements, weights were derived from the counting statistics.

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Registry No. **1a**, 115421-93-7; **1b**, 115421-94-8; **1c**, 115421-95-9; **1d**, 115422-09-8; **1e**, 115422-10-1; **1f**, 115421-96-0; **2a**, 115421-97-1; **2b**, 115421-98-2; **2c**, 115421-99-3; **2d**, 115422-00-9; **2e**, 115422-01-0; **2f**, 115422-02-1; **3a**, 115422-03-2; **3b**, 115422-04-3; **3c**, 115422-05-4; **3d**, 115422-06-5; **3e**, 115422-07-6; **3f**, 115422-08-7; **4**, 940-71-6; **7**, 104738-11-6; **8a**, 72474-25-0; **8b**, 72474-28-3; **8c**, 72474-27-2; **8d**, 72474-20-5; **8e**, 110718-21-3; **8f**, 84811-29-0; Me_3SiCH_2MgCl, 13170-43-9; Me_3SiCH_2Cl, 2344-80-1; C_2H_5MgCl, 2386-64-3; *i*-C_3H_7MgCl, 1068-55-9; *n*-C_4H_9MgCl, 693-04-9; C_6H_5MgCl, 100-59-4; *neo*-$C_5H_{11}MgCl$, 13132-23-5; *t*-C_4H_9MgCl, 677-22-5; Me_3SiCH_2I, 4206-

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67-1; *neo*-$C_5H_{11}Cl$, 753-89-9; $[(n\text{-}Bu)_3PCuI]_4$, 59245-99-7; CF_3CH_2OH, 75-89-8; CF_3CH_2ONa, 420-87-1.

Supplementary Material Available: C–H bond lengths (Tables XI and XII), H–C–X bond angles (Tables XIII and XIV), positional parameters for hydrogen atoms (Tables XV and XVI), selected least-squares planes and distances of atoms from those planes (Tables XVII and XVIII), and thermal parameters (Tables XIX and XX) (10 pages); observed and calculated structure factor amplitudes (Tables XXI and XXII) (60 pages). Ordering information is given on any current masthead page.

Notes

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Platinum(0) Complexes as Catalysts of Metal Carbonyl Substitution Reactions

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Phosphine-substituted metal carbonyls have often been prepared by methods involving thermal or photochemical replacement of a CO ligand, despite several commonly observed problems: low yields, mixtures of mono- to multi-substituted products, and long reaction times.[1] More recently, several new procedures[2] have been developed to promote CO substitution by other ligands under mild conditions. Among them is Me_3NO,[3] which oxidatively decarbonylates metal carbonyls, leading to a coordinatively unsaturated intermediate. Sodium benzophenone ketyl (BPK)[4,5] has been shown to catalyze CO substitution. Also, several transition-metal complexes induce catalytic CO displacement in metal carbonyls. These include $[CpFe(CO)_2]_2$,[6] $[CpMo(CO)_3]_2$,[7] $CoCl_2$,[8] PdO,[9] and $Fe_2(CO)_6(SMe)_2$.[10] In most of these reactions, there is evidence for electron-transfer catalysis (ETC) or it has been suggested that ETC is involved. We report here that the Pt(0) complexes $Pt(PPh_3)_4$ and Pt(dibenzylideneacetone)$_2$ (Pt(dba)$_2$) also catalyze the phosphine substitution of CO in mono-, di-, and trinuclear metal carbonyl complexes. These two catalysts offer a convenient, high-yield route to monosubstituted $M_x(CO)_{y-1}L$ complexes where L is a monodentate phosphine ligand.

Experimental Section

General Reagents and Procedures. All reactions were performed under prepurified N_2. Unless noted otherwise, reagent grade chemicals were used without further purification. Methylene chloride and hexanes were distilled from CaH_2 and stored under N_2 over type 4A molecular sieves. Benzene was distilled from sodium benzophenone under N_2.

The starting compounds, $W(CO)_6$, $Fe(CO)_5$, $CpMn(CO)_3$, $Re_2(CO)_{10}$, and $Ph_2PCH_2CH_2PPh_2$ (dppe) were purchased from Pressure Chemical Co. Other starting compounds, $CpFe(CO)_2I$,[11] $Re(CO)_5(CH_3)$,[12] $Pt(PPh_3)_4$,[13] and Pt(dba)$_2$,[14] were prepared as reported in the literature. The compound $Os_3(CO)_{12}$ was prepared from OsO_4 by a modification of a literature procedure[15] that was carried out in a 300-mL stainless steel pressure autoclave (Parr Model No. 4761).

Infrared spectra were recorded on a Perkin-Elmer 681 instrument. ^1H NMR spectra were recorded on a Nicolet NT-300 spectrometer. Electron-impact mass spectra were obtained by using a Finnigan 4000 GC-MS.

Reaction of Metal Carbonyls with PPh_3 in the Presence of $Pt(PPh_3)_4$. A solution of PPh_3 (1–2 equiv), the metal carbonyl compound (1 equiv) ($W(CO)_6$, $Fe(CO)_5$, $CpFe(CO)_2I$, $Re(CO)_5(CH_3)$, $CpMn(CO)_3$, $Re_2(CO)_{10}$ or $Os_3(CO)_{12}$), and $Pt(PPh_3)_4$ (0.1 equiv) was brought to reflux in 50 mL of benzene under an N_2 atmosphere. The reactions were monitored by changes in the IR spectra (2200–1600 cm^{-1}). At the end of the reaction (as established by the disappearance of the starting material), the solution was cooled to room temperature and the solvent removed under vacuum. The residue dissolved in CH_2Cl_2 was then passed through a silica-gel column (2.5 × 15 cm) with 1:1 CH_2Cl_2/hexanes as the eluant. The PPh_3-substituted products were collected. Recrystallization from CH_2Cl_2/hexanes gave the isolated products (percent yields in Table I), which were identified by their IR and ^1H NMR spectra (Table I). The catalyst, $Pt(PPh_3)_4$, was recovered. Also shown in Table I are results of control reactions where no Pt(0) catalyst was used.

Reaction of Metal Carbonyls with Ligands in the Presence of Pt(dba)$_2$. A 50-mL benzene solution containing a donor ligand (PPh_3, PPh_2Me, dppe, $P(OMe)_3$, or norbornadiene) (usually 1.5 equiv), a metal carbonyl ($Fe(CO)_5$ or $CpFe(CO)_2I$) (1 equiv), and Pt(dba)$_2$ (0.1 equiv) was refluxed in a Schlenk flask. The reaction was monitored by IR spectroscopy (2200–1600 cm^{-1}), and heating was continued until the reaction had gone to completion. The solvent was removed under vacuum; the residue dissolved in CH_2Cl_2 was chromatographed (2.5 × 15 cm) on silica gel with 1:1 CH_2Cl_2/hexanes as the eluent. The products were recrystallized from CH_2Cl_2/hexanes.

Results and Discussion

The substitution of one CO ligand in a variety of metal carbonyl complexes by PPh_3 is catalyzed by $Pt(PPh_3)_4$ (eq 1) in refluxing

$$M_x(CO)_y + PPh_3 \xrightarrow[\text{benzene}]{Pt(PPh_3)_4} M_x(CO)_{y-1}(PPh_3) + CO \quad (1)$$

$$M_x(CO)_y = W(CO)_6,\ Fe(CO)_5,\ CpFe(CO)_2I,\ Re(CO)_5(CH_3),\ Re_2(CO)_{10},\ Os_3(CO)_{12}$$

benzene. As summarized in Table I, the products are isolated in 70–98% yields and the $Pt(PPh_3)_4$ catalyst may be recovered nearly quantitatively. Under the conditions of the reactions, but in the absence of the catalyst, there is essentially no reaction. Only the monophosphine-substituted complexes are obtained even when

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