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Hexacoordinate Phosphorus. 5. Synthesis and Characterization of Neutral Phosphorus(V) Compounds Containing Substituted Bidentate Amidino Ligands Derived from Carbodiimides

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A series of neutral hexacoordinate (λ^6) phosphorus compounds (**1–8**) of the general formula $Cl_{4-n}(CF_3)_n\overline{PN(R)C(Cl)}NR$ (n = 0–3; R = cyclohexyl, isopropyl) have been prepared by an apparent carbodiimide insertion into a P–Cl bond of a pentacoordinate (λ^5) phosphorane. The six-coordinate nature of these derivatives is evidenced by their characteristic high-field ^{31}P NMR chemical shifts and is further substantiated by the crystal structure of $Cl_2(CF_3)_2\overline{PN(R)C(Cl)}NR$ (**5**), where R = cyclohexyl. Crystal data for **5**: monoclinic, space group $P2_1/c$ (No. 14), a = 8.548 (3) Å, b = 24.280 (8) Å, c = 10.571 (5) Å, β = 111.18 (3)°, V = 2045 Å^3, Z = 4. Final R and R_w values for **5** are 0.052 and 0.067, respectively. The molecular structure of **5** shows that the two nitrogen atoms of the chloroamidine ligand are equivalently bound to phosphorus (P–N = 1.843 (3), 1.837 (4) Å) with slightly elongated bond lengths relative to a normal P–N σ bond, that the chloroamidine ligand is essentially planar, and that the two Cl atoms and the carbodiimide framework atoms and the ipso carbon of the cyclohexyl substituents lie in the same plane about the λ^6-phosphorus atom. These λ^6-phosphoranes are not very reactive. Lithium phenyl substitutes at the chlorine on the ring of $Cl_4\overline{PN(R)C(Cl)}NR$ (**2**), and not on phosphorus, to give $Cl_4\overline{PN(Pr^i)C(Ph)}NPr^i$ (**9**), where R = isopropyl. Hydrolysis of **2** gave the phosphoryl compound with a monodentate ligand $Cl_2(O)P{-}N(Pr^i)C(Cl){=}NPr^i$ (**10**). A detailed characterization, using multinuclear NMR, infrared, and mass spectroscopic data, of all compounds is reported.

Introduction

Recently[1] we extended the range of known and structurally characterized[2–4] neutral compounds containing a six-coordinate phosphorus center by binding carbamate,[5,6] thiocarbamate,[5] or acetylacetone[1,2] units as bidentate chelate ligands to a five-coordinate phosphorus center. Structural characterization has shown the presence of the chelate ring and extended the limited examples provided earlier by $F_4P(acac)$[2] and $RF_3P(8\text{-oxyquinolyl})$[4] (R = F, Ph) and $Cl_4\overline{PN(R)C(Cl)}N(CH_3)$.[3c] All of these examples except for the latter are best formed by metathetical substitution of a halogen on a five-coordinate phosphorus PX_5 center with a bifunctional monovalent substituent by elimination of either HF or $(CH_3)_3SiX$:

$$F_5P + Hacac \rightarrow F_4P(acac) + HF \quad (1)$$

$$CH_3(CF_3)_3PX + (CH_3)_3SiOC(O)N(CH_3)_2 \rightarrow CH_3(CF_3)_3P(O_2CN(CH_3)_2) + (CH_3)_3SiX \quad (2)$$

As long as the phosphorus center is sufficiently acidic (or the donor site is sufficiently basic), the chelated form is obtained. Weakly basic ligands or weakly acidic phosphorus centers generate fluxional systems wherein the six-coordinated structure with the bidentate substituent is in equilibrium with the five-coordinated species in which the ligand is attached in its monodentate form.[7] The chelated derivatives containing the bidentate substituent thus create compounds that can traverse more complex reaction pathways by partial dissociation of one of the coordinating atoms of the bidentate ligand. In contrast, the well-known extensive series of $X_5P{\cdot}B$ donor–acceptor complexes[8] will lose the unique donor substituent if dissociative reaction occurs at the base site. The characteristics and behavior of the chelated systems may therefore provide additional illumination of the reactivity of highly coordinated phosphorus.

Compounds containing five- and six-membered chelate rings based on 8-oxyquinolyl and acac substituents, respectively, are generally unreactive.[1,2,4] The potentially more strained four-membered chelate rings formed from small-bite bidentate ligands have only been encountered in the few examples of carbamates,[5,6] benzamidines,[7] and the rather unexpected chloroamidine derivative $Cl_4\overline{PN(CH_3)C(Cl)}N(CH_3)$ formed from *N,N'*-dimethylurea and PCl_5.[3] Our carbamates were first prepared by an apparent insertion of CX_2 (X = O, S) into the P–N bond of $CH_3(CF_3)_3P{-}N(CH_3)_2$,[5] but further insight showed that the reaction involved preformed carbamate. The more general process described by eq 2 is therefore the superior synthetic route.[6] Some of the carbamates[6] were also fluxional in solution, providing examples of possible reactivity pathways involving the monodentate substituent attached to the lower coordinate phosphorus center, whereas the acac derivatives showed no evidence of this behavior.

Herein we report a novel preparative route for a series of neutral six-coordinate phosphorus compounds **1–8** (Figure 1) containing a chelated amidine substituent formed by an apparent carbodiimide insertion into a P–Cl bond of a λ^5-phosphorane to form the four-membered ring system.

Experimental Section

General Procedures. The (trifluoromethyl)phosphoranes CF_3PCl_4, $(CF_3)_2PCl_3$, $(CF_3)_3PCl_2$, and $CH_3(CF_3)_3PCl$ were prepared according to published methods.[9] The reactants PCl_5, dicyclohexylcarbodiimide, (DCC) and diisopropylcarbodiimide (DPC) were obtained from Aldrich and used without further purification. Solvents were dried and distilled before use. The ^1H, ^{19}F, and ^{31}P spectra were obtained using Bruker WP200, WP400, and WP80 spectrometers on $CDCl_3$ solutions (approximately 10% compound) in vacuum-sealed 5-mm NMR tubes. Mass spectra were recorded with an AEI MS-12 spectrometer operating at an ionizing voltage of 70 eV. Infrared spectra were recorded with a Polaris FTIR spectrometer using a 0.1-mm KBr solvent cell. All manipulations were carried out either on a high-vacuum line or in a glovebag under dry argon. Melting points were determined on samples sealed in melting point capillaries and are uncorrected.

Preparation of Tetrachloro(*N,N'*-dicyclohexylchloroamidino)phosphorus(V) (1) and Tetrachloro(*N,N'*-diisopropylchloroamidino)phos-

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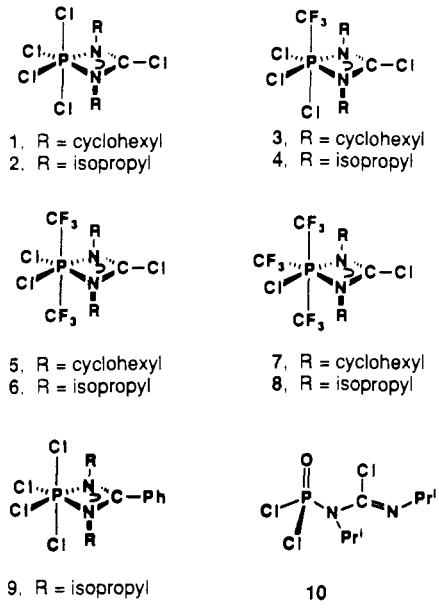


1, R = cyclohexyl
2, R = isopropyl
3, R = cyclohexyl
4, R = isopropyl
5, R = cyclohexyl
6, R = isopropyl
7, R = cyclohexyl
8, R = isopropyl
9, R = isopropyl
10

Figure 1. (Chloroamidino)phosphoranes (**1–8**) and the derivatives **9** and **10**.

phorus(V) (2). A sample of PCl_5 (ca. 0.5–1.5 g) was dissolved in CCl_4 (50 mL) under Ar in a round-bottomed flask. To this stirred solution an equivalent amount of DCC (a) or DPC (b) was slowly added by dry addition tube or syringe, respectively. The mixture was refluxed under Ar for 3 h and then cooled to room temperature. The solvent was removed in vacuum to leave a white solid (a) (mp 160–163 °C) for **1** (Anal. Calcd for $C_{13}H_{22}Cl_5N_2P$: C, 37.66; H, 5.35; Cl, 42.76; N, 6.76. Found: C, 37.68; H, 5.26; Cl, 42.64; N, 6.78. MS (*m/e* (relative intensity, % of strongest peak), identity): 378 (2.3), M − Cl; 242 (15.2), $ClCN_2C_{12}H_{22}$; 173 (7.6), PCl_4; 159 (21.9), $ClCN_2C_6H_{11}$; 101 (9.4), PCl_2; 83 (41.9), C_6H_{11}; 67 (24.9), C_5H_7; 55 (100), C_4H_7; 41 (91.9), CN_2) and (b) (mp 76–78 °C) for **2** (Anal. Calcd for $C_7H_{14}Cl_5N_2P$: C, 25.14; H, 4.22; Cl, 53.00; N, 8.38. Found: C, 25.75; H, 4.31; Cl, 50.94; N, 8.59. MS (*m/e* (relative intensity, % of strongest peak), identity): 299 (23.2), M − Cl; 173 (64.5), PCl_4; 126 (11.1), $CN_2C_6H_{14}$; 104 (43.9), $ClCN_2C_2H_4$; 83 (12.5), $CN_2C_3H_7$; 69 (100), CNC_3H_7; 43 (90.3), C_3H_7).

General Preparation of Chloro(trifluoromethyl)amidinophosphoranes. A sample of (ca. 0.5–3.5 mmol) DCC was weighed out into a glass reaction vessel or a sample of DPC was transferred by a syringe into a glass reaction vessel. Then CCl_4 (5 mL) was distilled in followed by an equivalent amount of the λ^5-chloro(trifluoromethyl)phosphorane. The vessel was sealed under vacuum and allowed to warm to room temperature. The bottom end of the vessel was placed in an oil bath and warmed to 100 °C for 3 h to establish reflux. After cooling to room temperature, the solvent was removed in vacuum to leave a white solid. Yields were 90% or greater.

(a) Trichloro(*N,N'*-dicyclohexylchloroamidino)(trifluoromethyl)phosphorus(V) (3). Mp: 163–165 °C. Anal. Calcd for $C_{14}H_{22}Cl_4F_3N_2P$: C, 37.52; H, 4.95; Cl, 31.64; N, 6.25. Found: C, 37.22; H, 4.95; Cl, 28.42; N, 6.12%. MS (*m/e* (relative intensity, % of strongest peak), identity): 411 (20.8), M − Cl; 379 (1.6), M − CF_3; 206 (84.8), CF_3PCl_3; 177 (35.6), $CN_2C_{10}H_{17}$; 151 (19.7), $CN_2C_8H_{15}$; 124 (100), $CN_2C_6H_{11}$; 101 (22.2), Cl_2P; 96 (20.9), NC_6H_{11}; 83 (82.2), C_6H_{11}; 69 (18), CF_3; 55 (15.2), C_4H_7; 41 (82.2), CN_2.

(b) Trichloro(*N,N'*-diisopropylchloroamidino)(trifluoromethyl)phosphorus(V) (4). Mp: 73–75 °C. Anal. Calcd for $C_8H_{14}Cl_4F_3N_2P$: C, 26.11; H, 3.83; Cl, 38.54; N, 7.61. Found: C, 26.01; H, 3.66; Cl, 38.59; N, 7.51. MS (*m/e* (relative intensity, % of strongest peak), identity): 333 (57.6), M − Cl; 299 (5.6), M − CF_3; 207 (84.2), Cl_3PCF_3; 173 (18.0), Cl_2PCF_3; 126 (40.3), $CN_2C_6H_{14}$; 111 (56.3), $CN_2C_5H_{11}$; 104 (19.2), Cl_2P; 69 (100), CF_3; 43 (19.7), C_3H_7.

(c) Dichloro(*N,N'*-dicyclohexylchloroamidino)bis(trifluoromethyl)phosphorus(V) (5). Mp: 154–157 °C. Anal. Calcd for $C_{15}H_{22}Cl_3F_6N_2P$: C, 37.40; H, 4.60; Cl, 22.08; N, 5.81. Found: C, 37.34; H, 4.68; Cl, 21.72; N, 5.88. MS (*m/e* (relative intensity, % of strongest peak), identity): 445 (1.0), M − Cl; 411 (5.5), M − Cl_2; 241 (9.6), $ClCN_2C_{12}H_{22}$; 205 (45.8), F_6C_2ClP; 163 (15.8), $CN_2C_9H_{15}$; 124 (17.9), $CN_2C_6H_{11}$; 101 (12.2), Cl_2P; 83 (63.6), C_6H_{11}; 69 (61.8), CF_3; 55 (100), C_4H_7; 41 (79.6), CN_2.

(d) Dichloro(*N,N'*-diisopropylchloroamidino)bis(trifluoromethyl)phosphorus(V) (6). Mp: 114–117 °C. Anal. Calcd for $C_9H_{14}Cl_3F_6N_2P$: C, 26.92; H, 3.15; Cl, 26.49; N, 6.98. Found: C, 26.70; H, 3.37; Cl, 26.24; N, 6.79. MS (*m/e* (relative intensity, % of strongest peak), identity): 365 (20.8), M − Cl; 331 (85.2), M − CF_3; 239 (40.7), $C_2F_9Cl_2P$; 205 (100), CF_3Cl_3P; 126 (39.5), $CN_2C_6H_{14}$; 111 (57.2), $CN_2C_5H_{11}$; 69 (80.6), CF_3; 43 (21.6), C_3H_7.

(e) Chloro(*N,N'*-dicyclohexylchloroamidino)tris(trifluoromethyl)phosphorus(V) (7). Mp: 148–150 °C. Anal. Calcd for $C_{16}H_{22}Cl_2F_9N_2P$: C, 37.30; H, 4.30; Cl, 13.76; N, 5.44. Found: C, 37.86; H, 4.35; Cl, 14.26; N, 5.62. MS (*m/e* (relative intensity, % of strongest peak), identity): 479 (4.9), M − Cl; 445 (26.4), $C_2F_6Cl_2PCN_2C_{12}H_{22}$; 363 (31.5), $C_3F_9ClCN_2C_6H_{11}$; 327 (39.2), $C_2F_6ClCN_2 - C_6H_{11}$; 273 (31.5), C_3F_9ClP; 239 (95.1), $C_2F_6Cl_2P$; 124 (13.3), $CN_2C_6H_{11}$; 83 (66.0), C_6H_{11}; 69 (77.5), CF_3; 55 (100), C_4H_7; 41 (72.5), CN_2.

(f) Chloro(*N,N'*-diisopropylchloroamidino)tris(trifluoromethyl)phosphorus(V) (8). Mp: 100–102 °C. Anal. Calcd for $C_{10}H_{14}Cl_2F_9N_2P$: C, 27.61; H, 3.24; Cl, 16.30; N, 6.44. Found: C, 27.65; H, 3.25; Cl, 16.31; N, 6.46. MS (*m/e* (relative intensity, % of strongest peak), identity): 399 (14.0), M − Cl; 365 (14.9), M − Cl_2; 273 (51.4), C_3F_9ClP; 239 (80.4), C_3F_9P; 126 (3.3), $CN_2C_6H_{14}$; 111 (15.1), $CN_2C_5H_{11}$; 69 (100), CF_3; 43 (76.9), C_3H_7.

Preparation of Tetrachloro(*N,N'*-diisopropylphenylamidino)phosphorus(V) (9). A sample of **2** (1.17 g, 3.49 mmol) was weighed out into a round-bottom flask and dissolved in diethyl ether. The solution was cooled to −78 °C in dry ice/acetone bath. A solution of phenyllithium (1.65 M, 2.22 mL, 3.58 mmol) was added dropwise over a period of 1 h. The reaction mixture was allowed to warm to room temperature for 3 h. A white precipitate (LiCl) formed and was allowed to settle. The solution was transferred by syringe to another flask, and the solvent was removed under vacuum, leaving a pale yellow solid (mp 82–84 °C). Anal. Calcd for $C_{13}H_{19}Cl_4N_2P$: C, 41.52; H, 5.09; Cl, 37.71; N, 7.45. Found: C, 41.81; H, 5.92; Cl, 34.94; N, 6.70. MS (*m/e* (relative intensity, % of strongest peak), identity): 305 (0.8), M − 2Cl; 262 (1.2), $Cl_2PNCC_6H_5NC_3H_7$; 235 (20.2), M − 4Cl; 219 (1.8), $Cl_2PNCC_6H_5N$; 203 (2.6), $C_3H_7NCC_6H_5NC_3H_7$; 126 (14.5), $C_3H_7NCNC_3H_7$; 111 (29.6), $C_3H_7NCNC_2CH_4$; 83 (22.7), C_3H_7NCN; 69 (100), C_3H_7NC; 43 (45.1), C_3H_7.

Preparation of (*N,N'*-diisopropylchloroamidino)phosphonic Dichloride (10). A sample of **2** (1.26 g, 3.77 mmol) was placed in a reaction vessel and dissolved in CCl_4. A sample of H_2O (0.069 g, 3.83 mmol) was added and the mixture stirred for 2 h at room temperature. The CCl_4 was removed under vacuum leaving a thick yellow liquid (bp 102 °C/0.5 mmHg). Calcd for $C_7H_{14}Cl_3N_2OP$: C, 30.08; H, 5.01; Cl, 38.05; N, 10.02. Found: C, 30.75; H, 5.14; Cl, 38.46; N, 10.03. MS (*m/e* (relative intensity, % of strongest peak), identity): 280 (0.2), M; 236 (0.2), M − C_3H_7; 152 (5.7), $ClPOC_3H_7NC$; 144 (4.6), Cl_2PONCN; 126 (22.4), $C_3H_7CNCC_3H_7$; 111 (36.5), $C_3H_7NCNC_2H_4$; 83 (10.2), C_3H_7NCN; 69 (100), C_3H_7NC.

X-ray Data Collection for 5. A clear, colorless crystal of $C_{15}H_{22}Cl_3F_6N_2P$ (**5**), having an irregular shape with the approximate dimensions of 0.2 × 0.4 × 0.4 mm, was mounted in a capillary under a nitrogen atmosphere and optically centered in the X-ray beam of an Enraf-Nonius CAD4 automated diffractometer. All intensity measurements were performed by using Mo Kα radiation (λ = 0.710 73 Å) with a graphite crystal, incident-beam monochromator.

The automatic peak search and reflection indexing programs[10] generated a preliminary unit cell. An explorative survey of the crystal by oscillation and Weissenberg photography led to the final choice of a monoclinic cell with the systematic absences of *h0l*, *l* odd, and *0k0*, *k* odd; the space group was chosen as $P2_1/c$ (No. 14).[11]

The cell constants and orientation matrix were obtained by a least-squares refinement of the setting angles of 25 reflections in the range $18.9 < \theta < 2.47°$. The unit cell parameters are given in Table I.

The intensity data were collected at room temperature (23 °C) by using a θ–2θ scan of fixed speed, 2.0° min^{-1} in θ. The scan range varied as a function of θ to compensate for α_1–α_2 wavelength dispersion: ω scan width = 1.00 + 0.35 tan (θ)°. Backgrounds for the peaks were measured by extending the scan 25% on each side; this gave a peak-to-background counting time ratio of 2:1. Intensity measurements were made out to a maximum 2θ of 60°. Two reflections were chosen as standard reflections and were remeasured after every 120 min of exposure time to check on crystal and electronic stability over the course of data collection. The intensities of these reflections decreased overall by 7.2% and 10.9% during the data collection, but no decay correction was employed.

X-ray Data Reduction. A total of 8936 reflections were collected, and Lorentz and polarization factors were applied: $I = r(S - 2B)/Lp$; $\sigma(I)$

(10) The diffractometer programs are those supplied by Enraf-Nonius for operation of a CAD4F diffractometer with some local modification by Dr. R. G. Ball.

(11) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1969; Vol. I.

Table I. Crystal Data and Details of Intensity Collection for $Cl_2(CF_3)_2P(DCC)Cl$ (**5**)

mol formula	$C_{15}H_{22}Cl_3F_6N_2P$
fw	481.68
space group	monoclinic, $P2_1/c$ (No. 14)
temp, °C	22
radiation (λ, Å)	Mo Kα (0.71073)
unit cell params	
a, Å	8.548 (3)
b, Å	24.280 (8)
c, Å	10.571 (5)
β, deg	111.18 (3)
V, Å^3	2045
Z	4
ρ_{calcd}, g cm^{-3}	1.564
linear abs coeff μ, cm^{-1}	2.99
final R, R_w, GOF[a]	0.052, 0.067, 2.14

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$; GOF $= [\sum w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$.

$= [r(S + 4B) + (0.041I)^2]^{1/2}/Lp$, where r is the scan rate, S is the total scan count, B is the total background count, and Lp is the combined Lorentz and polarization factor.

Structure Solution and Refinement. The positions of the P and Cl atoms were derived from a Patterson map, and the remaining non-hydrogen atoms were located from a difference Fourier map. Adjustment[12] of atomic parameters was carried out by full-matrix least-squares refinement on F_o, minimizing the function $\sum w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes and the weight w is given by $w = 4F_o^2/\sigma^2(F_o^2)$.

The neutral-atom scattering factors were calculated from the analytical expression for the scattering-factor curves.[13] The f' and f'' components of anomalous dispersion[14] were included in the calculations of all non-hydrogen atoms.

All hydrogen atoms were generated at idealized calculated positions by assuming a C–H bond length of 0.95 Å and the appropriate sp^3 geometries. These atoms were then included in the calculations with fixed, isotropic Gaussian parameters 1.2 times that of the attached atom and constrained to "ride" on this atom.

The refinement of the coordinates and isotropic U's for all non-hydrogen atoms was continued to convergence. At that stage, the data were corrected for absorption effects (and other systematic errors) by using a scheme based on the absorption surface (Fourier filtering) method of Walker and Stuart.[15] The maximum and minimum correction factors applied to F_o were 1.3278 and 0.5548. After rejection of the systematically absent reflections and averaging over $2/m$ symmetry (R_{merge} on F for all data is 0.219), there were 5935 reflections, of which 2540, having $I > 3\sigma(I)$, were used in the subsequent refinement. The refinement was continued with use of anisotropic Gaussian displacement parameters for the non-hydrogen atoms. One CF_3 group was found to be rotationally disordered and was split into two groups of partial occupancy, 0.6 in one group (F(11)–F(13)) and 0.4 in the other (F(14)–F(16)). In the final cycle 271 parameters were refined by using 2540 observations with $I > 3\sigma(I)$ with the largest and average shift/error less than 0.01. As a result, the goodness-of-fit was 2.14, $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.052$, and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2} = 0.067$. An analysis of R_w in terms of F_o, $(\sin\theta)/\lambda$, and various combinations of Miller indices indicated no unusual trends. The highest peak in the final difference Fourier map has a density of 0.32 (7) e Å^{-3}.

The complete positional and isotropic thermal parameters for compound **5** are given in Table II. Additional information is available as supplementary material.

Results and Discussion

The compounds with hexacoordinate phosphorus chelates (**1–8**) were prepared as air-stable, moisture-sensitive, colorless, crystalline solids with sharp melting points ranging from 70 to 165 °C in quantitative yields by reaction of the appropriate chlorophosphorane with the carbodiimide under reflux in CCl_4 for a few hours (eq 3). All were immediately identified as λ^6-phosphorus(V) compounds by their low-frequency (high-field) signals in the ^{31}P NMR spectra.

Table II. Positional[a] and Thermal[b] Parameters for All Non-Hydrogen Atoms in $Cl_2(CF_3)_2P(DCC)Cl$ (**5**)

atom	x	y	z	U_{eq}[c]
P	1478 (1)	1368.1 (5)	3505 (1)	4.15 (3)
Cl(1)	594 (2)	1686.5 (7)	4980 (1)	7.37 (5)
Cl(2)	−911 (1)	1254.6 (6)	1955 (1)	5.85 (4)
Cl(3)	6073 (1)	1112.4 (6)	3528 (1)	6.91 (5)
N(1)	3733 (4)	1401 (2)	4535 (3)	4.5 (1)
N(2)	2702 (4)	1112 (1)	2513 (3)	3.9 (1)
C(11)	4767 (5)	1581 (2)	5929 (4)	5.6 (2)
C(12)	5737 (7)	2098 (2)	5973 (5)	6.6 (2)
C(13)	6614 (7)	2284 (3)	7448 (6)	8.8 (2)
C(14)	7761 (7)	1841 (3)	8270 (6)	8.9 (3)
C(15)	6827 (9)	1308 (3)	8205 (6)	11.6 (3)
C(16)	5927 (8)	1121 (2)	6741 (5)	8.9 (3)
C(21)	2336 (5)	896 (2)	1131 (4)	4.9 (2)
C(22)	3040 (7)	330 (2)	1105 (5)	7.2 (2)
C(23)	2420 (7)	106 (3)	−338 (5)	8.8 (2)
C(24)	2851 (7)	490 (3)	−1281 (5)	8.8 (2)
C(25)	2215 (9)	1060 (3)	−1216 (5)	10.9 (3)
C(26)	2824 (8)	1276 (2)	229 (5)	9.3 (2)
C(1)	1572 (5)	2116 (2)	2862 (5)	5.4 (2)
C(2)	1272 (6)	641 (2)	4151 (4)	5.9 (2)
C(3)	4104 (5)	1208 (2)	3527 (4)	4.3 (1)
F(11)[d]	121 (6)	2341 (2)	2073 (6)	9.4 (2)
F(12)[d]	2546 (6)	2181 (2)	2163 (5)	9.7 (2)
F(13)[d]	2142 (7)	2469 (2)	3875 (5)	8.6 (2)
F(21)	−176 (4)	543 (1)	4304 (3)	9.8 (1)
F(22)	2425 (4)	517 (2)	5325 (3)	10.6 (1)
F(23)	1350 (4)	239 (1)	3306 (3)	9.5 (1)

[a] Values × 10^4. [b] Values × 10^2 in Å^2. [c] $U_{eq} = {}^1/_3\sum_{i=1}^{3} r_i^2$, where r_i are the root-mean-square amplitudes of the anisotropic Gaussian displacement parameters. [d] CF_3 group is disordered; partial population of 0.6 for atoms F(11)–F(13).

$$X_3PCl_2 + R\text{-}N{=}C{=}N\text{-}R \xrightarrow{\Delta,\ CCl_4} \text{(3)}$$

R = cyclohexyl or isopropyl; X = Cl or CF_3

The tetraalkylmonochlorophosphorane, $CH_3(CF_3)_3PCl$, did not react even after prolonged heating. The failure of this reaction was unexpected, considering that our previous experience showed that $CH_3(CF_3)_3PX$ (X = Cl, F) reacted readily with monovalent chelate precursors, such as acetylacetone[1] or $(CH_3)_3SiO_2CN(CH_3)_2$.[5,6] This result implies that the "insertion" reaction pathway is probably not dissociative and that steric hindrance around the central phosphorus might be interfering with the formation of the necessary six-coordinated phosphorus intermediate. This might arise because $CH_3(CF_3)_3PCl$ is more sterically hindered than $(CF_3)_3PCl_2$ or the other chlorophosphoranes used. It is also interesting that the successful reactions described by eq 3 give products that are parallel to those given by $MoCl_5$ and $ReCl_5$ with diisopropylcarbodiimide.[16]

These new compounds extend significantly the previously meagre list of chlorinated neutral λ^6-phosphorus compounds. Previous attempts to form chlorinated λ^6-phosphorus compounds from carbamates[5] and phosphorus(V) acetylacetonates[17] were not successful.

Structure of $Cl_2(CF_3)_2P(DCC)Cl$ (5). The structure of **5** (Figure 2) shows clearly the six-coordinate environment at phosphorus. The two CF_3 groups are located mutually trans to each other in the axial positions. Two mutually cis chlorine atoms and the chloroamidino chelating ligand occupy the radial positions.

(12) The computer programs used in this determination include the Enraf-Nonius Structure Determination Package., Version 3 (1985, Delft, The Netherlands) adapted for a SUN Microsystems 3/160 computer, as well as several locally written programs written by Dr. R. G. Ball.
(13) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974, Vol. IV, Table 2.2B (present distributor D. Reidel, Dordrecht, The Netherlands).
(14) Table 2.3.1 of ref 13.
(15) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *A39*, 158.
(16) Rajca, G.; Schwarz, W.; Weidlein, J.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1985**, *522*, 83.
(17) Burford, N.; Cavell, R. G. Unpublished observations.

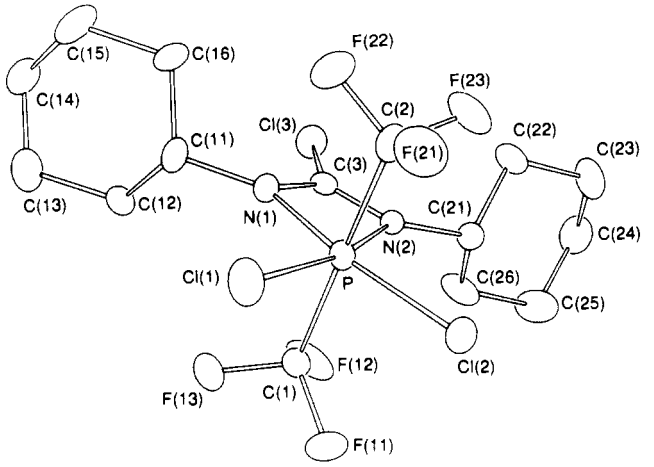


Figure 2. Perspective view of **5**, showing the atom-labeling scheme. Atoms are represented by Gaussian ellipsoids at the 30% probability level.

Table III. Selected Bond Distances and Angles for $Cl_2(CF_3)_2P(DCC)Cl$ (**5**)

Bond Distances[a,b]			
P-Cl(1)	2.110 (2)	C(2)-F(21)	1.326 (6)
P-Cl(2)	2.124 (2)	C(2)-F(22)	1.311 (5)
P-C(1)	1.950 (5)	C(2)-F(23)	1.340 (6)
P-C(2)	1.924 (6)	N(1)-C(3)	1.305 (6)
P-N(1)	1.841 (3)	N(2)-C(3)	1.308 (4)
P-N(2)	1.837 (4)	C(3)-Cl(3)	1.698 (5)
C(1)-F(11)	1.336 (6)	N(1)-C(11)	1.483 (5)
C(1)-F(12)	1.307 (8)	N(2)-C(21)	1.475 (5)
C(1)-F(13)	1.320 (7)		
Bond Angles[b,c]			
Cl(1)-P-Cl(2)	96.67 (8)	C(2)-P-N(1)	92.3 (2)
Cl(1)-P-C(1)	89.3 (2)	C(2)-P-N(2)	92.1 (2)
Cl(1)-P-C(2)	88.3 (2)	N(1)-P-N(2)	70.7 (2)
Cl(1)-P-N(1)	97.2 (1)	P-N(1)-C(3)	90.7 (2)
Cl(1)-P-N(2)	167.4 (1)	P-N(1)-C(11)	136.1 (3)
Cl(2)-P-C(1)	90.1 (1)	C(3)-N(1)-C(11)	133.1 (4)
Cl(2)-P-C(2)	88.2 (1)	P-N(2)-C(3)	90.8 (3)
Cl(2)-P-N(1)	166.2 (1)	P-N(2)-C(21)	136.5 (3)
Cl(2)-P-N(2)	95.9 (1)	C(3)-N(2)-C(21)	132.7 (4)
Cl(3)-P-C(2)	176.9 (2)	N(1)-C(3)-N(2)	108.2 (4)
Cl(3)-P-N(1)	90.0 (2)	N(1)-C(3)-Cl(3)	125.6 (3)
Cl(3)-P-N(2)	90.7 (2)	N(2)-C(3)-Cl(3)	126.2 (4)

[a] In Å. [b] Numbers in parentheses are estimated standard deviations in the least significant digits. [c] In degrees.

Relevant metrical parameters for **5** are given in Table III.

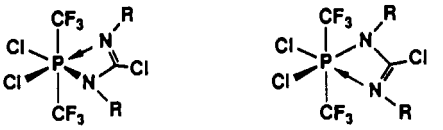
The structure of a related compound, $Cl_4PN(CH_3)C(Cl)N$-CH_3, prepared from PCl_5 and *N,N'*-dimethylurea has been previously reported.[3c] However, severe problems with hydrolysis of the crystal were encountered during data collection with the result that final structure was refined to an *R* factor of only 0.13.[3c] Detailed analysis of the structural features displayed in that case is not therefore warranted, and in particular the asymmetry of P-N bond lengths reported therein is not borne out by the present results. The amidino framework in **5** is, as expected, symmetrically bound to the phosphorus as it is to Mo[16] in the analogous Mo derivative. The framework of **5** is also similar to that of the acetylacetonate analogue of hexacoordinate phosphorus, F_2-$(CF_3)_2P(acac)$, which we have reported previously.[1]

As in the acetylacetonate analogue, placing the two CF_3 groups trans to each other and perpendicular to the radial plane of the molecule allows the relatively bulky CF_3 groups to avoid interaction with each other. All of the atoms in the radial section of the molecule are essentially coplanar with the largest deviation from the least-squares plane being 0.012 (5) Å for the C(3) atom in the four-membered ring. The CF_3 groups sitting above and below the phosphorus bend slightly away from the amidino ring side toward the radial chlorine atoms so as to form a C(1)-P-C(2) angle of 177.1 (3)°, which relieves interactions of the CF_3 groups with the ring. The large cyclohexyl groups are folded in an expected chair conformation and are positioned away from the phosphorus center, again avoiding interaction with other atoms within the molecule.

Compared to the acetylacetonate analogue, there is even greater deviation from the ideal octahedral arrangement around the phosphorus in **5**. The chelating amidino ligand subtends a very tight angle at phosphorus (70.7 (2)°) as a consequence of the constraints imposed by the formation of the four-membered ring whereas the more flexible acetylacetone ligand allowed a wider angle at phosphorus (95.4 (2)°). As a result of the squeezing of the chelate ligand in **5**, the chlorines spread out around the phosphorus, forming an angle of 96° instead of the ideal 90°. It is interesting to note that the N-P-N angle in the four-membered ring of **5**, 70.7 (2)°, is smaller than that in the λ^3-1,3 diaza-2-phosphetine cation $[(Pr^i)_2N-P-N(Me_3Si)C(Ph)N(SiMe_3)]^+$, 73.2°,[18] which was previously ranked the smallest intracyclic N-P-N angle for a four-membered phosphorus-containing heterocycle.[18] Our smaller angle is presumably the result of oxidation of the phosphorus to the five valent state in our compound. Geometrical features similar to those displayed by **5** have been previously observed in the neutral hexacoordinate phosphorus dimethylcarbamates, $F(CF_3)_3P(O_2CN(CH_3)_2)$[6] and $CH_3(C$-$F_3)_3P(O_2CN(CH_3)_2)$,[5] which also contain a bidentate ligand subtending a very small angle (72.4° and 69.9°, respectively) at phosphorus.

Both the P-Cl and the P-C bond distances are normal with mean values of 2.116 and 1.912 Å, respectively. The ring C-Cl distance (1.696 (6) Å) is very similar to the distance expected for a C-Cl single bond (1.70 Å) found in olefinic and aromatic compounds.[19] Although the C-N bonds joining the cyclohexyl groups to the nitrogen atoms are comparable to the average single-bond C-N distance of 1.45 Å, the C-N bonds in the chelate ring are significantly shorter (1.310 Å), indicating the presence of a delocalized double bond within the N-C-N ring system. Similar shortened C-N bond distances (1.34 Å) within the bidentate chelate ligand have also been reported for $[(Pr^i)_2N-P-N(Me_3Si)C(Ph)N(SiMe_3)]^+$.[18]

The most remarkable feature of this structure of **5** is the planarity of and presumably the electronic delocalization within this chelate ring. Compounds of this type can be represented by two resonance forms:



The ring C-N bond is a partial double bond, as evidenced by the fact that it is shorter than the typical CN single bond. In addition, the contribution of a dative N→P bond to the resonance structures is reflected in the relatively long P-N bond distance of 1.830 Å, compared to the expected P-N single-bond distance of 1.77 Å estimated from covalent radii[18] and the P-N single bond distance of 1.79 Å found for the amino N-P bond in $[(Pr^i)_2N-P-N-(Me_3Si)C(Ph)N(SiMe_3)]^+$.[18] P-N dative bonds in the simple base adducts $F_5P\cdot py$ (1.89 Å)[20] and $F_5P\cdot NH_3$ (1.849 Å)[21] are notably longer, and so the P-N bond character is suitably regarded as somewhere between a dative link and a P-N single bond. It is notable in all these cases that the amidine substituent is symmetrically bound to the phosphorus.

Nuclear Magnetic Resonance Spectra. The structures of **1-8** could readily be deduced from their ^1H, ^{19}F, and ^{31}P NMR spectra

(18) Roques, C.; Mazieres, M.-R.; Majoral, J.-P.; Sanchez, M.; Jaud, J. *Inorg. Chem.* **1989**, *28*, 3933.
(19) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.
(20) Sheldrick, W. S. *J. Chem. Soc., Dalton Trans.* **1974**, 1402.
(21) Storzer, W.; Schomburg, D.; Roschenthaler, G.-V.; Schmutzler, R. *Chem. Ber.* **1983**, *116*, 367.

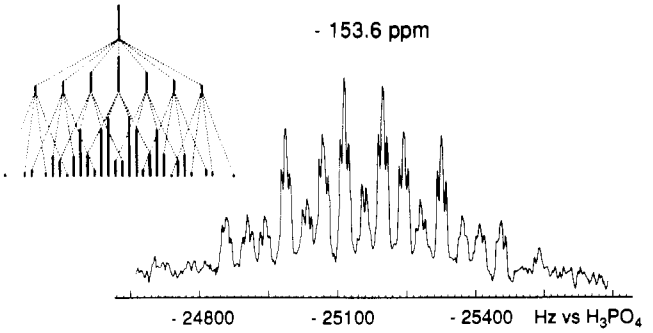


Figure 3. $^{31}P\{^1H\}$ 162-MHz NMR spectrum of $Cl(CF_3)_3P(DPC)Cl$ (**8**). Also shown is the evolution of the pattern of a septet ($^2J_{PF}$ = 128 Hz) of quartets ($^2J_{PF}$ = 83 Hz).

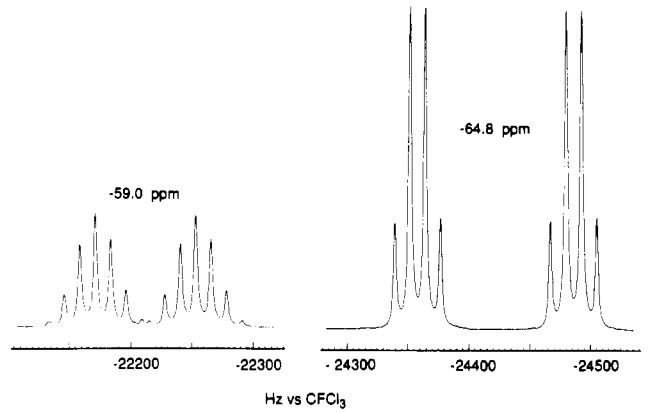


Figure 4. ^{19}F (376.5 MHz) NMR spectrum of $Cl(CF_3)_3P(DPC)Cl$ (**8**).

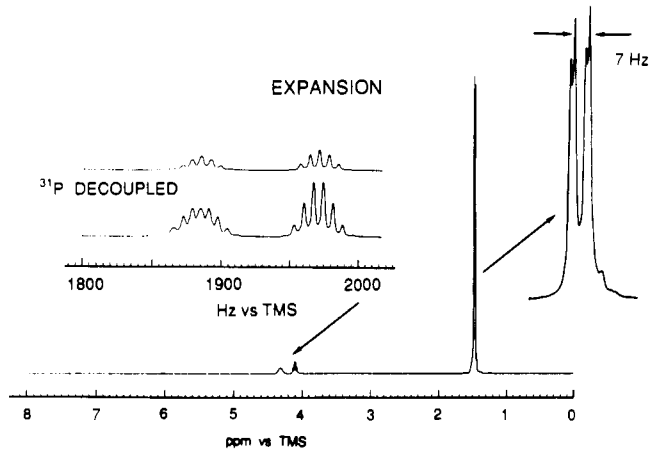


Figure 5. ^1H (400 MHz) NMR spectrum of $Cl(CF_3)_3P(DPC)Cl$ (**8**).

in solution. Spectra of **8** are shown in Figures 3–5. A summary of the NMR parameters of **1**–**8** is given in Table IV. Like the acetylacetonates[1] with hexacoordinate phosphorus centers, the chloroamidino derivatives are not fluxional at ordinary probe temperatures. The ^{31}P NMR spectra show, in all cases, chemical shifts at very low frequencies (−155 to −205 ppm) compared to the shifts for the five-coordinate precursors $(CF_3)_nPCl_{4-n}$ (n = 0–3) (−56 to −80 ppm), indicating the formation of a hexacoordinate phosphorus center.

Compounds **1** and **2** are clearly characterized by the presence of a triplet ($^3J_{PH}$) signal at −205 ppm in the ^{31}P NMR spectra, due to the nearest proton to phosphorus of the cyclohexyl or isopropyl group on each of the nitrogens of the chelating bidentate ligand.

As expected, **3** and **4** display a low-frequency quartet of triplets ($^2J_{PF}$ and $^3J_{PH}$, respectively) in the ^{31}P NMR spectra. The lone CF_3 group must necessarily lie in the axial position because there is only one phosphorus-coupled signal in the ^1H NMR spectra, indicating a symmetry plane orthogonal to the plane of the PNCN ring. It is notable that there is no evidence of isomerism in these cases whereas the carbamates and acetylacetonates clearly showed two isomers in their CF_3 derivatives, obviously one with an axial and one with a radial CF_3 group.[1,6] Those cases are not wholly comparable; the phosphorus has F not Cl substituents (the chlorophosphorus acac and carbamate derivatives could not be obtained),[1,6] and the preparative route is very different. The isomeric distribution may be kinetically controlled.

Table IV. NMR Parameters for Amidinophosphoranes and Their Derivatives

				coupling constants, Hz			
cmpd[a]	$\delta(^1H)$[b]	$\phi(^{19}F)$[c]	$\sigma(^{31}P)$[d]	$^3J_{PH}$	$^2J_{FP}$	$^3J_{HH}$	$^4J_{FF}$
1	4.12		−204.7[e]	34.6		12.0	
						3.8	
2	4.50[f]		−205.2[e]	34.8		7.0	
3	4.08	−68.7[g]	−181.7[h]	20.7	134.0	*i*	
4	4.50[j]	−69.1[g]	−181.8[h]	20.4	134.0	6.9	
5	3.91	−66.8[g]	−155.8[k]	10.2	170.5	11.9	
						4.0	
6	4.34[l]	−67.4[g]	−155.7[k]	10.0	171.6	7.0	
7	3.66	−64.5[m] (2)[n]	−154.9[o]	9.6	128.4 (ax)	12.0	12.6
		−58.7[p] (1)[n]			82.1 (rad)	4.0	
8	4.09[q]	−64.8[m] (2)[n]	−155.3[o]	9.2	128.4 (ax)	7.0	12.6
	4.30	−59.0[p] (1)[n]			82.9 (rad)		
9	4.53		−205.6[e]	36.0		7.2	
10	3.85		−10.5[g]	18.1		6.3	
	4.28					6.8	

[a] In $CDCl_3$. [b] Values for ^1H on carbon bound to nitrogen only; ppm relative to TMS. [c] ppm relative to $CFCl_3$. [d] ppm relative to 85% H_3PO_4. [e] Triplet. [f] CH_3 signal due to isopropyl methyl groups in a simple doublet, $^3J_{HH}$ = 7 Hz at 1.40 ppm. [g] Doublet. [h] Quartet of triplets. [i] Signal too broad to determine HH coupling. [j] CH_3 signal due to isopropyl methyl groups is a simple doublet, $^3J_{HH}$ = 6.9 Hz at 1.54 ppm. [k] Septet of triplets. [l] CH_3 signal due to isopropyl methyl groups is a simple doublet, $^3J_{HH}$ = 7 Hz at 1.42 ppm. [m] Doublet of quartets. [n] Relative intensity. [o] Septet of quartets of triplets. [p] Doublet of septets. [q] CH_3 signal due to isopropyl methyl groups is a doublet of doublets, $^3J_{HH}$ = 7.0 Hz (spacing ca. 0.005 ppm) at 1.45 ppm.

The ^{19}F spectra for **5** and **6** show a simple doublet in each case with very similar $^2J_{PF}$ values. Since the crystal structure of **5** shows equivalent axial CF_3 groups and since the analogous compounds $F_2(CF_3)_2P(O_2CN(CH_3)_2)$ and $F_2(CF_3)_2P(acac)$ also have, according to the solid-state structural determinations,[1,5] axially placed CF_3 groups and very similar, large values of $^2J_{PF}$ (164.3[5] and 163.4[1] Hz, respectively), it seems reasonable to assign to **6** the structure (Figure 1) in which both CF_3 groups are axial and equivalent.

The low-frequency chemical shifts of **7** and **8** in the ^{31}P NMR spectra also indicate hexacoordination about phosphorus. The phosphorus signals in **7** and **8** are split into a first-order septet of quartets with $^2J_{PF}$ coupling to three CF_3 groups in a 2:1 ratio of types; Figure 3 illustrates this coupling pattern. Without ^1H decoupling (Figure 3) additional proton coupling is also seen, with each peak in the septet of quartets appearing as a triplet due to $^3J_{PH}$ coupling to the CH protons of two isopropyl groups. The unsolved[22] solid-state structure of **7** is consistent in that there appears to be one equatorial and two axial CF_3 groups.

The ^{19}F NMR spectra of **7** and **8** show two signals in an intensity ratio of 2:1 with the expected doublet of quartets and

(22) X-ray diffraction data for **7** were collected by Dr. B. Vaartstra and Dr. M. Cowie, Department of Chemistry, University of Alberta, and refinement was attempted; however, **7** showed a space group ambiguity and severe disordering so refinement was not completed. However, it was clear from the structure even at an initial poorly refined stage that **7** contained a hexacoordinate phosphorus center with two axial CF_3 groups and one radial CF_3 group as depicted in Figure 1, and it is therefore similar to the analogous carbamates $F(CF_3)_3P(O_2NC(CH_3)_2)_6$ and $CH_3(CF_3)_3P(O_2NC(CH_3)_2)$.[5] As in **5**, the axial CF_3 groups in **7** sit above and below the radial plane formed by the third CF_3 group, the chlorine, and the chelated chloroamidino ligand. The cyclohexyl groups in **7** show the expected chair conformation observed for **5**. The radial CF_3 group and the radial Cl are positionally disordered and in addition all the CF_3 groups are, as usual, rotationally disordered. It is the former feature that blocks the structural refinement.

Table V. Infrared Absorption Frequencies (cm^{-1}) for Amidinophosphoranes and Their Derivatives[a]

1	2	3	4	5	6	7	8	9	10
2920 vs	2990 s	2960 vs	2970	2920 s	2980	2920 s	2975	2990 s	3200 br
2850 vs	2930	2880 s	2915	2845 s	2920	2810	2950	2930 vs	2982 s
1668	2880	2104	2850	1654	2860	2360	2900	2870 s	2944
1522 vs	1668	1679 s	1664	1516 vs	2330	2100	2845	1657 s	2875
1461	1528 vs	1519 vs	1524 vs	1462	1670	1654	2320	1526 vs	2536 br
1452 vs	1450	1467	1455	1452 s	1524 vs	1516 vs	1523 vs	1463	1682 vs
1369 s	1387	1452	1388	1366	1500	1487	1500 s	1453	1660 vs
1348	1366 s	1364	1368	1352	1465	1448	1461	1439	1611 vs
1327	1343	1351	1351	1268	1392	1370	1393	1386	1471
1289	1289	1258	1318	1174 s	1372	1339	1372	1369	1452
1261	1212 vs	1184	1212 s	1161 vs	1351	1256	1354	1343	1422
1181 s	1169	1156 s	1161 s	1131 vs	1211 s	1190 s	1206 s	1284 s	1400
1146	1131	1138	1145 s	1038	1166 vs	1174 vs	1186 vs	1236	1379
1080	1122 s	1121 s	1130 vs	1029	1137 vs	1166 vs	1168 vs	1212 s	1276 br vs
1047 s	931	1111 s	1121 vs	929	1128 vs	1143 vs	1143 vs	1152	1222 br
1024	699	1032	921	894	1068	1122 vs	1125 vs	1119 s	1167
946	654 s	1022	675	848	957	1078	1078	1027	1134
892	585	890	570 s	835	800	1028	919	1011	1118
839	533	708	520 s	693	793	1012	732	928	1079 s
814	517 vs	660		664	778	922	682 s	656	563 vs
	466 vs	550		552	772	887	570 s	614	
	438 vs	507 s		525 s	760	848	498 s	588	
		480 s		497 s	749	691	472	556 s	
				455 s	680	671 s		546 s	
					556	562 s		539 s	
					531 s	499 s		516 vs	
					495 vs	463		465 s	
					460 s			434 vs	

[a] In CCl_4 with 0.1-mm KBr solvent cell. vs = very strong; s = strong; br = broad.

doublet of septets structure, respectively (Figure 4). The larger signal intensity show a larger $^2J_{PF}$ coupling constant of about 128 Hz compared with the remaining CF_3 signal, which has a $^2J_{PF}$ coupling constant of about 82 Hz. Again, associating the larger $^2J_{PF}$ values with axial CF_3 groups as above, we assign to **7** and **8** the structures in which two CF_3 groups are axial and one CF_3 group is radial.

The ^1H NMR spectrum of **8** has two distinct and separate phosphorus-coupled signals arising from unique isopropyl CH protons trans to a CF_3 group and trans to a Cl. The two methyl signals at 1.5 ppm upon expansion reveal two doublets corresponding to two different isopropyl group environments. Further downfield (4.0–4.5 ppm region) there are two smaller individual multiplets (Figure 5), which correspond to the central proton on each of the two isopropyl groups. Each of these signals is a septet in the ^{31}P-decoupled spectrum, as expected for coupling to six equivalent methyl protons. In the ^{31}P-coupled spectrum, each signal becomes an overlapping doublet of septets. The isopropyl groups on the ligand are therefore inequivalent, which strongly reinforces the assignment of the illustrated structures for **7** and **8** (Figure 1) in which there are two axial CF_3 groups and one radial CF_3 group.

Mass Spectra. None of the compounds containing highly coordinated phosphorus (**1–9**) show a parent peak in the mass spectrum. All have major fragments identified as being due to a loss of one Cl from the parent molecule. Many of the other major peaks can be attributed to the loss of the chloroamidino ligand and successive losses of Cl and CF_3 groups.

Infrared Spectra. The infrared absorption frequencies for compounds **1–9** are given in Table V. Of particular interest are the N=C stretching absorptions compared to the free ligands and related metal derivatives in Table VI. The large reduction in the N=C stretching frequency for the chelated amidino ligand (~1520 cm^{-1}) compared to the free ligand (~2100 cm^{-1}) supports the proposed structures. Partial double-bond character is assigned to the bonding of the central carbon with the two coordinating nitrogens because the stretching frequency falls between the double (~2100 cm^{-1}) and the single (~1350 cm^{-1}) carbon–nitrogen bond stretching frequency values. The analogous Mo and Re amidino derivatives[16] showed higher N=C absorption frequencies (1644 and 1640 cm^{-1}, respectively), suggesting that there is a greater N=C double-bond character in these cases, which in turn suggests

Table VI. C=N Stretching Frequencies

compd	freq, cm^{-1}	compd	freq, cm^{-1}
DCC[b]	2133	$Cl_4Re(DPC)Cl$[16]	1640
1	1522	**2**	1528
3	1519	**4**	1524
5	1516	**6**	1523
7	1516	**8**	1523
DPC[c]	2112	**9**	1526
$Cl_4Mo(DPC)Cl$[16]	1644	**10**	1682

[a] In CCl_4 with 0.1-mm KBr solvent cell. [b] DCC = dicyclohexylcarbodiimide; DPC = diisopropylcarbodiimide.

that the amidino ligand is more strongly bonded to P than to the metals. This is also reflected in the shorter P–N bond length found in **5** (average 1.839 (4) Å) compared to the relatively long Mo–N bond length in $Cl_4Mo(DPC)Cl$ (2.079 (4) Å).[16] No significant difference was found in the N=C absorption frequencies between $Cl_4(DPC)Cl$ (**2**) (1528 cm^{-1}) and $Cl_4P(DPC)Ph$ (**9**) (1526 cm^{-1}), but as the number of CF_3 groups increases about the phosphorus, making it a stronger Lewis acid, the N=C frequency becomes slightly smaller, implying a further strengthening of the P–N bond.

Reactivity of λ^6-Amidinophosphoranes. As an illustration of the hydrolytic sensitivity of the compounds **1–8**, exposure of $Cl_4P(DPC)Cl$ (**2**) to the moisture in the air (or alternatively hydrolyzed directly with 1 equiv of water) gave $Cl_2(O)P$–(DPC)Cl (**10**) (eq 4).

$$Cl_4P(DPC)Cl\ (\mathbf{2}) + H_2O \rightarrow Cl_2\overset{O}{\overset{\|}{P}}\text{-}(DPC)Cl\ (\mathbf{10}) + 2HCl \quad (4)$$

This and related phosphoryl compounds are typically yellow liquids with properties characteristic of λ^4-phosphorus compounds. The characteristic ^{31}P NMR chemical shift of −10.5 ppm ($Cl_3P{=}O$ resonates at −2 ppm)[23] confirms the phosphoryl identity, and further this phosphorus signal is a doublet indicating coupling to only one isopropyl group. The ^1H NMR spectrum indicates two different isopropyl groups, only one of which is coupled to the phosphorus. As it is a compound with a four-coordinate center, **10** shows a parent ion in the mass spectrum.

(23) Corbridge, D. E. C. *Phosphorus*, 2nd ed.; Elsevier Scientific Publishing Co.: Amsterdam, 1980.

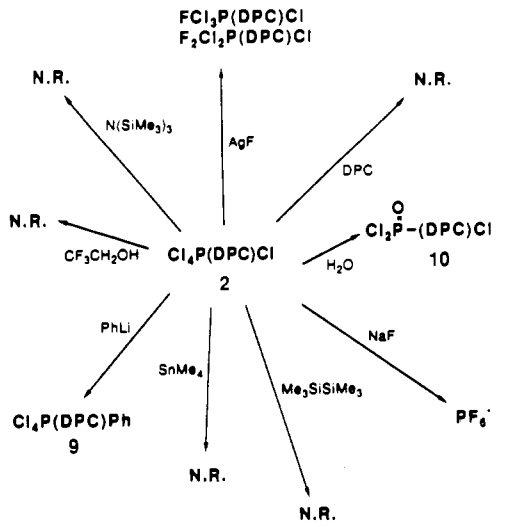


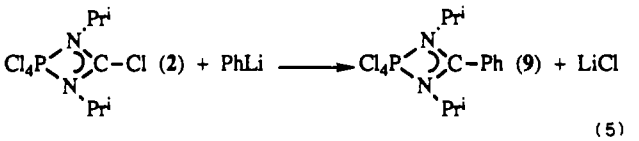
Figure 6. Reactions of $Cl_4P(DPC)Cl$ (**2**).

Apart from their sensitivity to water, these hexacoordinate phosphorus compounds (**1–8**) are rather unreactive. Nucleophilic and electrophilic reactivities were evaluated for the prototypical **2** with a series of reagents (Figure 6). The results illustrate that **2** is resistant to simple substitution at chlorine on phosphorus. The lack of reactivity of these compounds is remarkable when compared to their five-coordinate precursors and strongly implies that the reaction pathway is associative and that the intermediate cannot be accessed because of the difficulty of expanding the coordination at phosphorus to seven.

Dissociative mechanisms involving the phosphorus center of **2** would involve either a ring opening or a removal of a chlorine atom to form the λ^5-phosphorus intermediates $Cl_4P(DPC)Cl$ or $Cl_3P(DPC)Cl^+Cl^-$, respectively, and the resistance of **2** to simple nucleophilic substitution, coupled with the fact that, in contrast to the case for carbamates, the NMR spectra yield no evidence of fluxional behavior (in compounds **3–8**), indicates that the five-coordinate intermediate is also not easily accessed, which in turn implies that the four-membered chelate ring in these molecules is very stable to ring opening.

Under vigorous conditions, fluorine can be substituted for chlorine in a metathesis reaction of **2** with AgF. The reaction is not complete so the result is a mixture of **2**, $Cl_3FP(DPC)Cl$, and $Cl_2F_2P(DPC)Cl$. The use of other fluorinating agents, such as NaF, resulted in the complete fluorination to PF_6^- with no evidence for the formation of any intermediate species.

Phenyllithium led to substitution of the chlorine on the ring and not of the chlorines on phosphorus (Figure 7 and eq 5), indicating that normal C–Cl reactions can be accomplished at the central ring carbon. The product of this reaction is a chelated benzamidino derivative of P(V), which is also accessible from benzamidine and PX_5.[7]



(5)

The ^{31}P NMR spectrum of **9** indicates the presence of a hexacoordinate phosphorus center with a low-frequency signal resonating as a triplet at −205.6 ppm. The $^3J_{PH}$ coupling to both isopropyl groups indicates that both nitrogens are still bound to the phosphorus. The ^1H NMR spectrum of **9** shows two equivalent isopropyl groups (coupled to phosphorus), implying a symmetrical compound, and one phenyl group (no phosphorus coupling). Together the ^1H and ^{31}P NMR spectra indicate **9** to be the structure shown in Figure 1, wherein the phenyl group is attached to the ring carbon.

Conclusion

A series of neutral hexacoordinate phosphorus compounds (**1–8**) containing a strained amidino four-membered ring have been characterized. The X-ray crystal structure of $Cl_2(CF_3)_2P(DCC)Cl$ (**5**) shows a six-coordinate environment around phosphorus with two mutually trans axial CF_3 groups, which are orthogonal to the plane of the chelating ring (Figure 2). Solution-state NMR data are completely consistent with this formulation and also suggest that no fluxionality occurs. The solid-state structure of $Cl(CF_3)_3P(DCC)Cl$ (**7**) could not be solved, but limited evidence was obtained in supported of the six-coordinate geometry around the phosphorus with two axial CF_3 groups and one radial CF_3 group. Again solution NMR spectra provided strong support for this structure.

The neutral hexacoordinate phosphorus compounds exemplified by the simple model compound $Cl_4(DPC)Cl$ (**2**) are not particularly reactive except toward water and nucleophilic substitution at the ring carbon. The chlorine substituents on P are strongly resistant to simple nucleophilic substitutions (Figure 6). Phenyllithium reacts with **2** with substitution of chlorine on the chelating ring (not the phosphorus), which further demonstrated the substitutional inertness of the phosphorus center in these hexacoordinate phosphorus systems. Inert behavior is to be expected if the coordination number of phosphorus cannot be expanded beyond six, if the chlorine substituents are strongly bound, and if the bidentate ligand does not dissociate readily. All these conditions would appear to be satisfied here.

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Supplementary Material Available: Tables S1–S5, listing experimental details of the structure determination, complete positional and thermal parameters, derived hydrogen positions, and complete bond distances and angles (6 pages); a table of calculated and observed structure factors (31 pages). Ordering information is given on any current masthead page.