Chemistry of Diazaphospholephosphines. 1. Preparation of Substituted 4-(Phosphino)-2,5-dimethyl-2*H*-1,2,3σ^2-diazaphospholes, Bifunctional Phosphines with Dicoordinate and Tricoordinate Phosphorus(III) Centers. Chromium(0) and Molybdenum(0) Difluorophosphine Complexes

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An improved preparation of 4-(dichlorophosphino)-2,5-dimethyl-2*H*-1,2,3σ^2-diazaphosphole (**1**) is described. Replacement of the two chlorine substituents with two fluorine (**2**), dimethylamino (**3**), diethylamino (**4**), bis(*n*-propyl)amine (**5**), pyrazole (**9**), 3,5-dimethylpyrazole (**10**), 2,2,2-trifluoroethoxy (**11**), phenoxy (**12**), pentafluorophenoxy (**13**), 2,6-difluorophenoxy (**14**), and pentafluorobenzoxy (**15**) substituents has been accomplished to create a large suite of potentially bifunctional phosphorus(III) ligands with two- and three-coordinate P centers spanning a range of basicity and steric bulk at the exo-phosphorus center. Bulky secondary amines (such as diisopropylamine, dibenzylamine, and iminodibenzyl) replaced only one chlorine atom to give asymmetric 4-(chloroaminophosphino)-2,5-dimethyl-2*H*-1,2,3σ^2-diazaphospholes (**6**, **7**, and **8**, respectively). The asymmetric substitution creates a diastereotopic center in both **6** and **7** which is observed as fluxional NMR behavior at room temperature. Similar diastereotopic induced behavior was observed in the substituent methylene protons of **11**. Coordination studies of the fluorinated phosphole (L = **2**) with Cr(0) and Mo(0) gave $Cr(CO)_5L$ (**16**), *cis*-$Mo(CO)_4L_2$ (**17**), and *fac*-$Mo(CO)_3L_3$ (**18**) (where L = 4-(difluorophosphino)-2,5-dimethyl-2*H*-1,2,3σ^2-diazaphosphole). The fluoro ligand displays a behavior which is similar to that of PF_3 and phosphites.

Introduction

Two trivalent phosphorus centers of contrasting structure and chemical nature are found in the diazaphospholephosphines, a dicoordinate (σ^2) endocyclic and a tricoordinate (σ^3) exocyclic phosphorus atom. These compounds are of considerable interest particularly with respect to their differential oxidation and/or coordination reactivity. A convenient precursor, 4-(dichlorophosphino)-2,5-dimethyl-2*H*-1,2,3σ^2-diazaphosphole (**1**), is easily synthesized,[1−4] and subsequent replacement of the chlorine substituents on the exocyclic (σ^3) phosphorus would allow the development of an extensive chemistry of this ligand system. Herein we report conversion of **1** to the difluoro analogue and also to a selection of amino and alkoxo derivatives which modify the electronic and steric character of the ligand. In the present study we employed simple and bulky amines (observing in the latter steric inhibition of substitution), aryloxy groups, and other electron-withdrawing (e.g., perfluorinated) alkoxo groups which resist the Arbuzov rearrangement,[5−8] because we were interested in accessing electronegative substituents which do not hydrolyze as do fluorine and chlorine. The resultant aryl/alkoxy compounds, in general, have physical properties which are intermediate between those of the halide and the amino analogues. The coordination chemistry of the system is of interest, and some examples of the difluorophosphine system are reported herein. Limited complexation results have been reported previously for Cr, Fe, Pd, and Pt[4,9−12] including some examples of phosphole formation from ylides and diphosphenes.[12,13]

Experimental Section

Experimental manipulations were performed under an atmosphere of dry argon using standard Schlenk techniques. Deuterated solvents, $CDCl_3$ and CD_2Cl_2, were distilled over P_2O_5 and stored over molecular sieves under argon before use. All other solvents were dried and freshly distilled prior to use; diethyl ether was distilled from sodium−benzophenone, hexane from sodium, and acetonitrile from P_2O_5 (then stored over CaH_2). Nuclear magnetic resonance spectra were recorded on Bruker WH-200 and WH-400 spectrometers using the deuterium signal of the solvent as both the reference and the signal lock. Respective operating frequencies were ^1H = 200.133 and 400.135 MHz, ^{13}C = 50.323 and 100.614 MHz, ^{31}P = 81.015 and 161.977 MHz, and ^{19}F = 188.313 and 376.503 MHz. External ^{13}C and ^1H standards were $SiMe_4$ and, for ^{31}P, 85% H_3PO_4. $CFCl_3$ was used as solvent, internal

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reference, and internal lock for ^{19}F NMR. Positive shifts lie downfield in all cases. NMR spectra were simulated using PANIC[14] and/or gNMR[15] software. Chemical ionization (CI) mass spectra were recorded using an AEI MS50 spectrometer exciting with ammonia at 16 eV. Low-resolution mass spectra (electron impact, EI) were recorded at 16 or 70 eV on an AEI MS50 spectrometer. Infrared spectra were recorded as CH_2Cl_2 casts on KBr cells using a Nicolet 7199 infrared spectrometer. Elemental analyses were performed by the Microanalytical Services Laboratory at the University of Alberta. Melting points were determined on samples in sealed melting point capillaries and are uncorrected.

Commercial reagents: 15-Crown-5, 2,5-dimethylpyrazole, *p*-fluorophenol, methyl hydrazine, 2,4,6-tri-*tert*-butylaniline, phenol, pentafluorophenol, pentafluorobenzyl alcohol, phosphorus trichloride, pyrazole, pentafluorobenzonitrile, $Mo(CO)_6$, $Cr(CO)_6$ (Aldrich), *N*,*N*-dimethylaminotrimethylsilane (Petrarch), sodium fluoride, and sodium azide (Fisher) were used as received. The amines (*tert*-butylamine (Mallinckrodt), diethylamine (Aldrich), dipropylamine (J. T. Baker), diisopropylamine (Aldrich)) were redistilled from KOH before use. *p*-Toluidine (J. T. Baker) was resublimed, and 2,2,2-trifluoroethanol (Alpha) was redistilled over 4 Å molecular sieves before use. $Mo(CO)_4$(nbd) was prepared as described in the literature.[16]

1. Synthesis of 4-(Dichlorophosphino)-2,5-dimethyl-2*H*-1,2,3σ^2-diazaphosphole (1). The literature preparation[1] of **1** was slightly modified. Acetone methylhydrazone (50 mL) was added over a period of 45 min to a 500 mL round bottom flask containing a large excess of phosphorus trichloride (250 mL) cooled to −60 °C and kept under argon. When the addition was complete, the solution was allowed to warm slowly to room temperature (22 °C). The mixture was then refluxed for a period of 2 days. The reaction mixture was then stored at −40 °C for a period of 2 days. The solution was filtered under argon and excess phosphorus trichloride removed *in vacuo*. Distillation under argon gave **1** as a colorless to pale yellow liquid, which was again filtered under argon to remove any of the hydrogen chloride adduct which had crystallized in the distilled material. Yields ranged from 66.4 to 83.6 g (50−63%). Bp = 90−95 °C/2 Torr. NMR ($CDCl_3$): $^{31}P\{^1H\}$, P(σ^2), δ 248.5 (d, $^2J_{PP}$ 79 Hz); P(σ^3), δ 158.1 (d, $^2J_{PP}$ 79 Hz).[1]

2. Preparation of 4-(Difluorophosphino)-2,5-dimethyl-2*H*-1,2,3σ^2-diazaphosphole (2). To a suspension of NaF (11.80 g, 0.281 mol) in 50 mL of acetonitrile (with 5 drops of 15-crown-5) at room temperature (22 °C) was added 4-(dichlorophosphino)-2,5-dimethyl-2*H*-1,2,3σ^2-diazaphosphole (**1**) (10.0 mL, 70.5 mmol) by means of a syringe. The suspension was then refluxed for 24 h, and the resultant solution was filtered through Celite and washed (2 × 5 mL) with acetonitrile. Distillation under argon gave **2** (bp = 172 °C/720 Torr.) as a colorless liquid, which was best stored at −40 °C (yield 9.84 g, 76.7%). Calcd for $C_4H_6F_2N_2P_2$: C, 26.39; H, 3.32; N, 15.39. Found: C, 26.09; H, 3.30; N, 15.46. MS (CI, *m*/*z*): 183 (M + 1, 100). IR: (neat, cm^{-1}): ν(P−F) 805 (s), 780 (s). NMR ($CDCl_3$): $^{31}P\{^1H\}$, P(σ^2), δ 255.0 (dt, $^2J_{PP}$ 107 Hz, $^3J_{PF} \approx 30$ Hz); P(σ^3), δ 208.8 (dt, $^2J_{PP}$ 107 Hz, $^1J_{PF}$ 1169 Hz); ^1H, C−CH_3 δ 2.50 (s), N−CH_3 δ 4.00 (d, $^3J_{\sigma^2PH}$ 10.7 Hz); $^{13}C\{^1H\}$, C−CH$_3$ δ 14.79 (d, $^3J_{PC}$ 17 Hz), N−CH$_3$ δ 41.51 (d, $^2J_{\sigma^2PC}$ 19 Hz), P−C^4−P δ 135.17 (dd, $^1J_{\sigma^3PC}$ 35 Hz, $^1J_{\sigma^3PC}$ 6 Hz), N−C^5−CH$_3$ δ 157.21 (dd, $^2J_{\sigma^2PC}$ 5 Hz, $^2J_{\sigma^3PC}$ 18 Hz); ^{19}F, δ −89.33 (dd, $^1J_{\sigma^3PF}$ 1169 Hz, $^3J_{\sigma^2PF}$ 34 Hz).

3. Preparation of 4-(Bis(dimethylamino)phosphino)-2,5-dimethyl-2*H*-1,2,3σ^2-diazaphosphole (3). A solution of *N*,*N*-dimethylaminotrimethylsilane (23.0 mL, 0.144 mol) in 25 mL of dichloromethane was added dropwise to a solution of **1** (10.0 mL, 70.5 mmol) in 75 mL of dichloromethane at 0 °C. When the addition was complete, the solution was allowed to warm to room temperature (22 °C) and stirring was continued for 24 h, during which time the solution became light yellow. The precipitate was removed by filtration. Solvent and excess *N*,*N*-dimethylaminotrimethylsilane were removed in vacuo, to leave a light yellow liquid, **3**, which was then distilled at 93−96 °C/0.6 Torr (yield 13.9 g, 84.8%). Calcd for $C_8H_{18}N_4P_2$: C, 41.38; H, 7.81; N, 24.13. Found: C, 41.25; H, 7.36; N, 24.21. MS (CI, *m*/*z*): 233 (M + 1, 100). IR (neat, cm^{-1}): ν(P−N) 713 (s), 656 (s), ν(N−C) 969 (s), 950 (s). NMR ($CDCl_3$): $^{31}P\{^1H\}$, P(σ^2), δ 243.2 (d, $^2J_{PP}$ 33 Hz); P(σ^3), δ 86.9 (d, $^2J_{PP}$ 33 Hz); ^1H, C−CH_3 δ 2.10 (s), P(σ^2)−N−CH_3 δ 3.80 (d, $^3J_{\sigma^2PH}$ 7.2 Hz), P(σ^3)−N−CH_3 δ 2.10 (s); $^{13}C\{^1H\}$, C−CH$_3$ δ 14.24 (d, $^3J_{PC}$ 4 Hz), P(σ^2)−N−CH$_3$ δ 40.65 (d $^2J_{\sigma^2PC}$ 17 Hz), P−C^4−P δ 150.95 (dd, $^1J_{\sigma^2PC}$ 54 Hz, $^1J_{\sigma^3PC}$ 9 Hz), N−C^5−CH$_3$ δ 155.68 (dd, $^2J_{\sigma^2PC}$ 7 Hz, $^2J_{\sigma^3PC}$ 19 Hz), P(σ^3)−N−CH$_3$ δ 40.65 (d, $^2J_{\sigma^3PC}$ 17 Hz).

4. Preparation of 4-(Bis(diethylamino)phosphino)-2,5-dimethyl-2*H*-1,2,3σ^2-diazaphosphole (4). A solution of **1** (10.0 mL, 70.5 mmol) in 100 mL of ether was added dropwise to a solution of diethylamine (32.0 mL, 309.3 mmol) in 250 mL of ether at 0 °C, during which time a precipitate of $Et_2NH{\cdot}HCl$ formed immediately. The mixture was allowed to slowly warm to room temperature (22 °C), and stirring was continued for 1 day. The precipitate was removed by filtration. Solvent and excess diethylamine were removed in vacuo, to leave a yellow liquid, **4**, which was distilled at 125−128 °C/0.06 Torr (yield 15.5 g, 76.4%). Calcd for $C_{12}H_{26}N_4P_2$: C, 49.99; H, 9.09; N, 19.43. Found: C, 49.82; H, 9.03; N, 19.60. MS (CI, *m*/*z*): 289 (M + 1, 100). IR (neat, cm^{-1}): ν(P−N) 717 (s), 663 (s), ν(N−C) 1013 (s), 967 (s). NMR ($CDCl_3$): $^{31}P\{^1H\}$, P(σ^2), δ 242.5 (d, $^2J_{PP}$ 29 Hz); P(σ^3), δ 77.9 (d, $^2J_{PP}$ 29 Hz); ^1H, C−CH_3 δ 2.27 (s), P(σ^2)−N−CH_3 δ 3.90 (d, $^3J_{\sigma^2PH}$ 6.8 Hz), N−CH_2−CH$_3$ δ 3.02 (dt, $^3J_{\sigma^3PH}$ 9.8 Hz, $^3J_{HH}$ 6.9 Hz), N−CH$_2$−CH_3 δ 0.97 (t, $^3J_{HH}$ 6.9 Hz); $^{13}C\{^1H\}$, C−CH$_3$ δ 14.68 (d, $^3J_{PC}$ 5 Hz), P(σ^2)−N−CH$_3$ δ 42.52 (d, $^2J_{\sigma^2PC}$ 17 Hz), P−C^4−P δ 153.16 (dd, $^1J_{\sigma^2PC}$ 55 Hz, $^1J_{\sigma^3PC}$ 9 Hz), N−C^5−CH$_3$ δ 155.54 (dd, $^2J_{\sigma^2PC}$ 7 Hz, $^2J_{\sigma^3PC}$ 21 Hz), P(σ^3)−N−CH$_2$−CH$_3$ δ 42.45 (d, $^2J_{\sigma^3PC}$ 23 Hz), P(σ^3)−N−CH$_2$−CH$_3$ δ 14.39 (s).

5. General Preparations of Bulky Amino Derivatives (5−10). The procedure described above in 4. was followed. To prepare the diethyl derivative above, a twofold excess of the amine sufficed to sequester the evolved HCl. In the cases of the bulkier *n*-propylamine, pyrazole, and 3,5-dimethylpyrazole, 1 equiv of triethylamine was used instead of an excess of the substituting base. Thus the disubstituted products 4-(bis(di(*n*-propyl)amino)phosphino)-2,5-dimethyl-2*H*-1,2,3σ^2-diazaphosphole (**5**), 4-(dipyrazolephosphino)-2,5-dimethyl-2*H*-1,2,3σ^2-diazaphosphole (**9**), and 4-(bis(3,5-dimethylpyrazole)phosphino)-2,5-dimethyl-2*H*-1,2,3σ^2-diazaphosphole (**10**) were prepared. The reactions with the very bulky amines (isopropylamine, dibenzylamine, and iminodibenzyl) gave the monosubstituted products: 4-(chloro(di(isopropyl)amino)phosphino)-2,5-dimethyl-2*H*-1,2,3σ^2-diazaphosphole (**6**), 4-(chloro(dibenzylamino)phosphino)-2,5-dimethyl-2*H*-1,2,3σ^2-diazaphosphole (**7**), 4-(chloro(iminodibenzyl)phosphino)-2,5-dimethyl-2*H*-1,2,3σ^2-diazaphosphole (**8**), respectively. For the isopropylamine reaction, a second equivalent of the amine was used. For dibenzylamine 1 equiv of triethylamine was used and the iminodibenzyl reaction was carried out with 1 equiv of DBU as the additional base. Details are given in the Supporting Information.

6. Preparation of Alkoxy Derivatives (11−15). (a) A typical procedure is described for 4-(bis(2,2,2-trifluoroethoxy)phosphino)-2,5-dimethyl-2*H*-1,2,3σ^2-diazaphosphole (**11**). Adding a solution of **1** (2.5 mL, 18 mmol) in 25 mL of ether dropwise to a solution of 2,2,2-trifluoroethanol (2.6 mL, 36 mmol) and triethylamine (5.0 mL, 38 mmol) in 125 mL of ether at 0 °C gave immediately a precipitate of $Et_3N{\cdot}HCl$. The solution was allowed to warm slowly to room temperature (22 °C), and stirring was continued for 1 day. The precipitate was removed by filtration. The solvent, excess trifluoroethanol, and triethylamine were removed in vacuo, to leave **11** as a white solid, which was recrystallized from hexane, stored at −10 °C for 1 day, and then sublimed at 65−70 °C/0.1 Torr (yield 5.5 g, 89.6%). Calcd for $C_8H_{10}F_6N_2O_2P_2$: C, 28.09; H, 2.95; N, 8.19. Found: C, 27.40; H, 2.92; N, 8.06. MS (EI, −*m*/*z*): 342 (M, 100), 259 (M−CH_2CF_3, 45). IR (CH_2Cl_2 cast, cm^{-1}): ν(P−O) 1175 (s). NMR ($CDCl_3$): $^{31}P\{^1H\}$, P(σ^2), δ 247.3 (d (broad), $^2J_{PP}$ 25 Hz); P(σ^3), δ 168.1 (ds, $^2J_{PP}$ 25 Hz, $^4J_{PF}$ 4 Hz); ^1H, C−CH_3 δ 2.48 (dd, $^4J_{\sigma^2PH}$ 0.8 Hz, $^4J_{\sigma^3PH}$ 0.8 Hz), P(σ^2)−N−CH_3 δ 4.02 (d, $^3J_{\sigma^2PH}$ 7.9 Hz), P(σ^3)−N−O−CH_2CF$_3$ δ 2.41 (m), δ 2.09 (m); $^{13}C\{^1H\}$, C−CH$_3$ δ 14.81 (d, $^3J_{\sigma^3PC}$ 6 Hz), P(σ^2)−N−CH$_3$ δ 41.54 (d, $^2J_{\sigma^2PC}$ 18 Hz), P−C^4−P δ 146.44 (dd, $^1J_{\sigma^2PC}$ 59 Hz, $^1J_{\sigma^3PC}$ 29 Hz), N−C^5−CH$_3$ δ 156.73 (dd, $^2J_{\sigma^2PC}$ 6 Hz, $^2J_{\sigma^3PC}$ 23 Hz), P(σ^3)−O−CH$_2$−CF$_3$ δ 63.30 (dq, $^2J_{\sigma^3PC}$ 8 Hz, $^2J_{FC}$ 36 Hz), P(σ^3)−

(14) *Parameter Adjustment in NMR by Iteration Calculation (PANIC)*; Brüker Instrument Co.: Karlsrühe, Germany.
(15) Spectra simulated with gNMR (4.0) by Budzelaar, G. M., Cherwell Scientific Publishing, Oxford, 1997.
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O−CH_2−CF_3 δ 123.49 (dq, $^3J_{\sigma^3PC}$ 7 Hz, $^1J_{FC}$ 278 Hz); ^{19}F, δ −75.70 (ddq, $^4J_{\sigma^3PF}$ 35 Hz, $^6J_{\sigma^2PF}$ 2.2 Hz, $^3J_{FH}$ 8.4 Hz).

(b) A similar procedure, carried out with phenol, pentafluorophenol, 2,6-difluorophenol, and 2,3,4,5,6-pentafluorobenzyl alcohol gave 4-(bis-(phenoxy)phosphino)-2,5-dimethyl-2*H*-1,2,3σ^2-diazaphosphole (**12**), 4-(bis(pentafluorophenoxy)phosphino)-2,5-dimethyl-2*H*-1,2,3σ^2-diazaphosphole (**13**), 4-(bis(2,6-difluorophenoxy)phosphino)-2,5-dimethyl-2*H*-1,2,3σ^2-diazaphosphole (**14**), and 4-(bis(2-(2,3,4,5-pentafluorophenyl)-ethoxy)phosphino)-2,5-dimethyl-2*H*-1,2,3σ^2-diazaphosphole (**15**), respectively. Details are given in the Supporting Information.

7. Preparation of Metal Complexes of the Difluoro Ligand 2. (a) Preparation of Cr(CO)$_5$(2) (16). A Schlenk flask containing a solution of $Cr(CO)_6$ (0.475 g, 2.2 mmol) in 100 mL of THF immersed in an ice bath was photolyzed (450 W mercury lamp) for 1.5 h (monitored by IR). Liquid **2** (0.30 mL, 2.2 mmol) was then added to the solution via syringe. The solution was stirred overnight at room temperature (22 °C), during which time the color gradually changed from orange to greenish-yellow. The solvent was removed in vacuo, to leave a greenish-yellow solid, which was then redissolved in 10 mL of diethyl ether and filtered through Celite. The resultant bright yellow solution was concentrated to ∼1 mL and stored at −40 °C for 24 h, to give yellow crystals of **16**: yield 0.58 g (70%); mp 52−55 °C. Calcd for $C_9H_6CrF_2N_2O_2P_2$: C, 28.90; H, 1.62; N, 7.49. Found: C, 28.99; H, 1.87; N, 7.75. IR (CH_2Cl_2 cast, cm^{-1}): ν(CO) 2079 (m), 1938 (vs). MS (FAB, *m*/*z*): 374 (M, 100). NMR ($CDCl_3$): ^{31}P{^{1}H}, (second order: P(σ^2), δ 257.2 (d, broad), $^2J_{PP}$ 120 Hz (long-range PF coupling unresolved); P(σ^3), δ 249.8 (dt, $^2J_{PP}$ 120 Hz) spectral simulation[15] gives $^2J_{PP}$ 120 Hz, $^1J_{PF}$ 1150 Hz, and $^3J_{PF}$ −10.0 Hz); ^{1}H, C−CH_3 δ 2.57 (s), P(σ^2)−N−CH_3 δ 4.05 (d, $^3J_{\sigma^2PH}$ 8.3 Hz); ^{13}C{^{1}H}, C−CH_3 δ 15.48 (s), P(σ^2)−N−CH_3 δ 41.76 (d, $^2J_{\sigma^2PC}$ 18.6 Hz), P−C^4−P δ 150.56 (dd, $^1J_{\sigma^2PC}$ 12 Hz, $^1J_{\sigma^3PC}$ 6 Hz), N−C^6−CH_3 δ 155.29 (s), CO δ 204.50 (s), CO δ 208.41 (d, slightly broadened, $^2J_{PC}$ 40 Hz); ^{19}F, δ −39.78 (second order, see coupling constants given under ^{31}P data).

(b) Attempted Preparation of Mo(CO)$_5$(2). Photolyzing a THF solution of $Mo(CO)_6$ in a Schlenk flask in a similar fashion to that described above followed by treatment with **2** under the same conditions gave a light brown solid which, according to the ^{31}P{^{1}H} NMR spectrum, was not the desired complex.

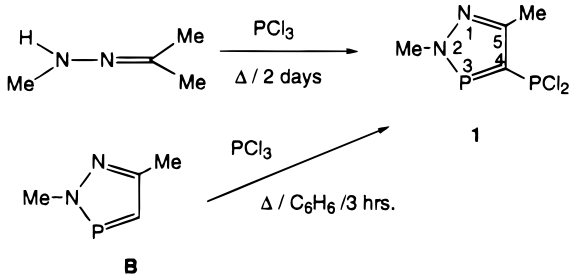
(c) Preparation of *cis*-Mo(CO)$_4$(2)$_2$, (17). A solution of the phosphole (**2**) (0.50 mL, 3.60 mmol) in 10 mL of dichloromethane was added dropwise at room temperature to a solution of Mo(nbd)-$(CO)_4$ (0.540 g, 1.80 mmol) in 15 mL of dichloromethane, and the reaction mixture was stirred for 12 h at room temperature (22 °C). The solution was concentrated to ∼5 mL, and hexane was added until the solution became slightly turbid. The solution was stored at −40 °C overnight, whereupon the off-white powder, **17**, precipitated: yield 0.69 g, 66.7%; mp 78−80 °C dec. Calcd for $C_{12}H_{12}F_4MoN_4O_4P_4$: C, 25.19; H, 2.11; N, 9.79. Found: C, 25.00; H, 1.97; N, 9.72. MS (FAB, *m*/*z*): 572 (M, 25). IR (CH_2Cl_2 solution, cm^{-1}): ν(CO) 2056 (m), 1974 (m), 1952 (vs). NMR ($CDCl_3$): ^{31}P{^{1}H), P(σ^2), δ 259.7 (broad, second order, $^2J_{PP}$ 146 Hz); P(σ^3), δ 223.0 (second order), $^1J_{PF}$ 1091 Hz); ^{1}H, C−CH_3 δ 2.57 (s), P(σ^2)−N−CH_3 δ 4.05 (d, $^3J_{\sigma^2PH}$ 8.3 Hz); ^{13}C{^{1}H}, C−CH_3 δ 15.51 (s), P(σ^2)−N−CH_3 δ 41.75 (d, $^2J_{\sigma^2PC}$ 17 Hz), P−C^4−P δ 151.34 (dd, $^1J_{\sigma^2PC}$ 12 Hz, $^1J_{\sigma^3PC}$ 6 Hz), N−C^5−CH_3 δ 154.32 (s), CO δ 208.32 (s), CO δ 212.35 (d, $^2J_{PC}$ 35 Hz). ^{19}F: δ −42.91 (second order).

(d) Preparation of *fac*-Mo(CO)$_3$(2)$_3$, (18). A solution of $Mo(CO)_6$ (0.50 mL, 3.60 mmol) in 25 mL of acetonitrile was refluxed for a period of 24 h; during this time the solution turned yellow. A solution of the phosphole (**2**) (1.7 mL, 12.2 mmol) in 5 mL of acetonitrile was then added dropwise at room temperature (22 °C) to the $Mo(MeCN)_3(CO)_3$ solution, which was then stirred for 12 h at room temperature. The solution was then concentrated to ∼2 mL and stored at −25 °C for 2 days, whereupon pale yellow needles of **18** formed: yield 1.1 g, 45.2; mp 123 °C dec. Calcd for $C_{15}H_{18}F_6MoN_6O_3P_6$: C, 24.81; H, 2.50; N, 11.57. Found: C, 24.75; H, 2.55; N, 11.62. MS (FAB, *m*/*z*): 726 (M, 15). IR (CH_2Cl_2 solution, cm^{-1}): ν(CO) 2011 (s), 1945 (s). NMR ($CDCl_3$): ^{31}P{^{1}H}, P(σ^2), δ 257.85 (d, broad, $^2J_{PP}$ 132 Hz); P(σ^3), δ 224.60 (second order); ^{1}H, C−CH_3 δ 2.57 (s), P(σ^2)−N−CH_3 δ 4.05 (d, $^3J_{\sigma^2PH}$ 8.3 Hz); ^{13}C{^{1}H}, C−CH_3 δ 15.48 (s), P(σ^2)−N−CH_3 δ 41.67 (d, $^2J_{\sigma^2PC}$ 19 Hz), P−C^4−P δ 150.92 (dd, $^1J_{\sigma^2PC}$ 11 Hz, $^1J_{\sigma^3PC}$ 6 Hz), N−C^5−CH_3 δ 153.68 (s), CO δ 209.65 (d, $^2J_{P\sigma^3C}$ 37 Hz); ^{19}F (second order), δ −42.92.

Results and Discussion

1. The Dihalogenated Phosphinephospholes. (a) Preparation of the Dichloro-diazaphosphole (1). There are two published routes (Scheme 1) to 4-(dichlorophosphino)-2,5-dimethyl-2*H*-1,2,3σ^2-diazaphosphole (**1**),[2,3] either via condensation of acetone methylhydrazone with an excess of phosphorus trichloride[2] or, alternatively, via reaction of previously prepared 2,5-dimethyl-2*H*-1,2,3σ^2-diazaphosphole with phosphorus trichloride.[3] The first approach is the most generally useful because the methylhydrazone condensation reaction naturally progresses to the 4-substituted phosphino-phosphole when excess PCl_3 is used. The details of this reaction were briefly described in the original publication,[2] but it was not made clear that in the second step of the process, wherein the desired phosphole is separated by distillation, concurrent sublimation of the initially formed hydrochloride salt from the reaction vessel into the condenser occurs thus contaminating the phosphinodiazaphosphole product. To minimize this contamination we used excess phosphorus trichloride and maintained longer reflux times. Furthermore it also proved effective to crystallize most of the intermediate hydrochloride out of the reaction mixture before beginning the distillation step. These modifications substantially improved the yield.

Scheme 1. Synthetic routes to 4-(Dichlorophosphino)-2,5-dimethyl-2*H*-1,2,3σ^2-diazaphosphole (**1**)[2,3] [a]

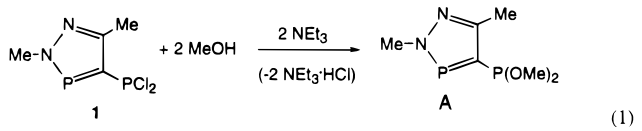


[a] The ring atom labels used herein are also indicated.

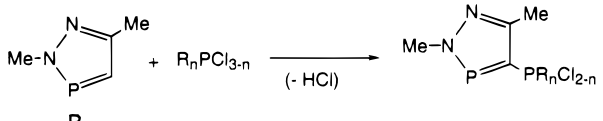
The two different phosphorus centers are clearly distinguished in the ^{31}P{^{1}H} NMR spectra; **1** shows a downfield signal at δ 249.0 ppm for the cyclic σ^2P center and a second, equal intensity signal at δ 157.6 ppm, due to the exocyclic σ^3P center. Each signal is split into a doublet with a $^2J_{PP}$ value of 79 Hz. Throughout this study, NMR proved to be an effective tool for characterizing all of the materials synthesized, and the ^{31}P and ^{13}C spectra especially proved to be highly diagnostic of structure and substitution because of diagnostic coupling constants as well as characteristic shift values. The ^{1}H NMR spectrum of **1** showed the imino methyl group protons at 4.03 ppm with coupling to both phosphorus centers ($^3J_{\sigma^2PH}$ 8.0 Hz, $^5J_{\sigma^3PH}$ 0.9 Hz). The resonance for the methyl group in the 5 position in the ring (on carbon) at 2.51 ppm also coupled to both of the phosphorus centers ($^4J_{\sigma^2PH}$ 2.1 Hz, $^4J_{\sigma^3PH}$ 1.4 Hz). Additional supporting information was obtained from ^{1}H and ^{13}C NMR spectroscopy. Details are given in the Supporting Information.

Exocyclic methoxy, methyl, and phenyl phosphine derivatives of **1** have been previously reported.[4] 4-(Dimethoxyphosphino)-2,5-dimethyl-2*H*-1,2,3σ^2-diazaphosphole (**A**) was obtained from **1** and methanol in the presence of triethylamine (eq 1). The methyl and phenyl derivatives were prepared differently: by treating the diazaphosphole **B** with the corresponding chlorophosphines (eq 2).[4] These reactions provided rather low (6−

36%) yields. Lithiation reactions were complex because the σ^2P and the 4 ring position are attacked.[17]



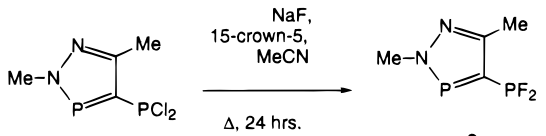
1 A (1)



B

n = 1, R = Me, Ph
n = 2, R = Ph (2)

(b) Synthesis of 4-(Difluorophosphino)-2,5-dimethyl-2*H*-1,2,3σ^2-diazaphosphole (2). Fluorination of **1** to 4-(difluorophosphino)-2,5-dimethyl-2*H*-1,2,3σ^2-diazaphosphole (**2**) in yields over 80% was easily effected with sodium fluoride in acetonitrile in the presence of a small amount of 15-crown-5 (eq 3), a procedure which is well established for fluorination of chlorophosphines.[18]



1 2 (3)

The fluorinated phosphole, **2**, is a volatile, colorless liquid with a boiling point of 172 °C under argon. It is slightly air-sensitive and best stored under argon at −40 °C, but even then, it occasionally became yellow over time; for pure material it is advisable to conduct a repurification, and this is conveniently done by a simple trap-to-trap distillation under vacuum with the receiving flask cooled to −25 °C. The impurities are apparently less volatile. The characteristic phosphorus−fluorine stretching frequencies at 805 and 780 cm^{-1} for **2** are slightly lower than the corresponding frequencies in PF_3 at (890 and 864 cm^{-1}) or $PhPF_2$ (974 and 865 cm^{-1}).[19] The $^{31}P\{^1H\}$ NMR spectrum of **2** showed the expected two sets of resonances coupled to each other ($^2J_{PP}$ 107 Hz) and also to both fluorine atoms on the σ^3P, yielding, for each phosphorus signal, the pattern of a doublet of triplets (Figure 1). The two-bond phosphorus−phosphorus coupling for fluoride **2** is larger than that of the chloride **1** ($^2J_{PP}$ 78 Hz) and may reflect an increase in the s character in the σ^3P bonding induced by the greater electronegativity of fluorine. The three-coordinate (σ^3) exocyclic upfield phosphorus signal (208.8 ppm) was sharp, but the endocyclic two-coordinate (σ^2) diazaphosphole phosphorus downfield resonance (255.0 ppm) was unexpectedly very broad in contrast to the relatively normal line width generally displayed by this signal.

This marked difference in the σ^2P and σ^3P spectral line widths for **2** prompted an evaluation of the ^{31}P NMR spin relaxation times (T_1) of the phosphorus nuclei. Relaxation times of 3.49 s for σ^3P and 8.64 s for σ^2P were determined (Figure 2); both values lie within the typical range of 2−20 s for trivalent phosphorus.[20] The σ^3P relaxation time in particular is appropriate for normal PX_3 (X = halogen) environments, which is usually 3−6 s. We have not found comparative literature T_1 values for the two-coordinate phosphorus center. If, however, the T_1 values

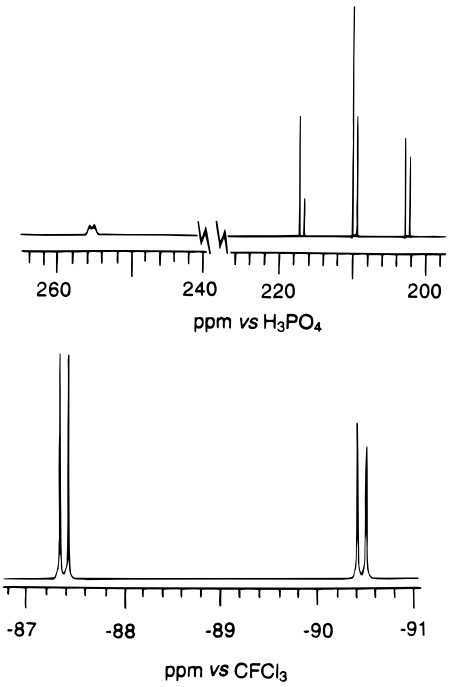


Figure 1. $^{31}P\{^1H\}$ NMR (81.015 MHz) (top) and ^{19}F NMR (188.31 MHz) (bottom) spectra of 4-(difluorophosphino)-2,5-dimethyl-2*H*-1,2,3σ^2-diazaphosphole (**2**) in $CDCl_3$.

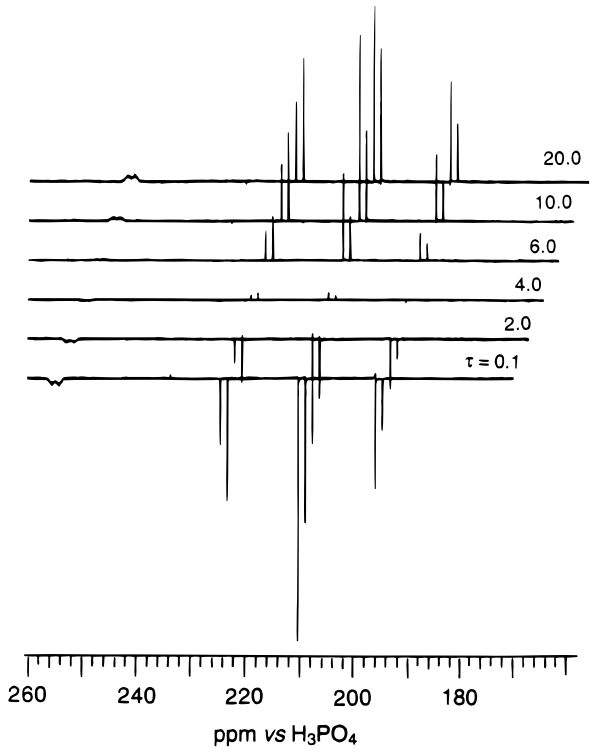


Figure 2. Stacked plot of $^{31}P\{^1H\}$ NMR spectra (81.015 MHz) obtained at different delay intervals (τ = 0.1, 0.2, 0.4, 0.6, 10.0, 20.0 s) to determine the T_1 values for 4-(difluorophosphino)-2,5-dimethyl-2*H*-1,2,3σ^2-diazaphosphole (**2**) in $CDCl_3$.

(17) Rösch, W.; Regitz, M. *Synthesis* **1984**, 591−593.
(18) Neda, I.; Fischer, A.; Jones, P. G.; Schmutzler, R. *Phosphorus, Sulfur Silicon Relat. Elm.* **1993**, *78*, 271−287.
(19) Corbridge, D. E. C. The Infrared Spectra of Phosphorus Compounds. In *Topics in Phosphorus Chemistry*; Grayson, M., Griffith, E. J., Eds.; Interscience Publishers: New York, NY, 1969; Vol. 6; pp 235−365.
(20) Tebby, J. C. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; VCH Publishers, Inc.: Deerfield Beach, FL, 1987; Vol. 8, pp 1−60.

in this system relate in a fashion similar to those of aromatic and aliphatic carbons in a compound such as ethylbenzene, where the aromatic carbons have values of ~18−23 s, the aliphatic methyl carbon has a value of ~7 s, and the ipso carbon has a much larger value of ~72 s,[21] we would expect the T_1 value for the ring σ^2P center to be much larger than that for the exocyclic σ^3P center. However, the relaxation time value for the σ^2P center in **2** is not that much greater than the value obtained for the σ^3P center, and both values lie within the typical phosphine range. Thus we conclude that the σ^2P center and the σ^3P center do not differ significantly in their NMR characteristics so the T_1 measurements have not indicated the reason for the broadness. Because of the broad line character, the fluorine couplings were not well resolved in the σ^2P signal; they could, however, be obtained from sharp ^{19}F spectra.

Interestingly, the chemical shift of the σ^3P unit of **2** is similar to that of $PPhF_2$ (208.3 ppm) and both of these compounds show a substantially different ^{31}P chemical shift relative to phosphorus trifluoride (98 ppm).

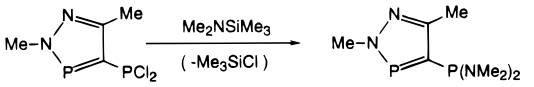
The ^{19}F NMR signal of **2**, at −89.3 ppm, was split by both phosphorus centers (Figure 1) to give a doublet of doublets pattern. The fluorine peaks were sharp, revealing clearly the coupling of the fluorine to the σ^2P unit ($^3J_{PF}$ 34 Hz). The one-bond $^1J_{PF}$ coupling with the σ^3P center (1169 Hz) has a typical value.[22]

The 2-methyl group on the nitrogen at δ 4.00 in the ^{1}H NMR spectrum of **2** showed less extensive coupling than is observed in **1**. These protons are coupled only to the σ^2P center ($^3J_{\sigma^2PH}$ 10.7 Hz). The resonance for the 5-methyl group in the case of **2** did not show coupling to either of the phosphorus centers, in contrast to **1**, where this long-range coupling was clearly visible. The ^{13}C{^{1}H} NMR spectrum of **2** showed extensive couplings to all carbon nuclei.

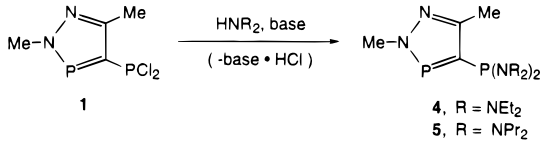
The fluorinated exocyclic σ^3P center is less basic and therefore less nucleophilic than normal phosphines, and so reactions which are inherently nucleophilic[23] should be inhibited. Iodomethane did not react with **2** to form a phosphonium salt, nor was the dicoordinate phosphorus center affected. In this respect this fluorophosphinephosphole behaves similarly to halogenated (especially fluorinated) CF_3 phosphines.[24]

2. Synthesis and Properties of Amino Phosphino Diazaphospholes. Placing amino substituents on the exocyclic phosphine should increase the basicity of this center especially when there are large alkyl substituents on the nitrogen. Steric constraints can also be introduced with bulky substituents. The 4-(diaminophosphino)-2,5-dimethyl-2*H*-1,2,3σ^2-diazaphospholes **3**−**5** are readily synthesized by a variety of replacement reactions on **1** using either silylated amines (eq 4) or secondary amines in the presence of a base (eq 5). In the latter case the "base" may be the same as or different from the attacking amine, and for the bulkier amines, particularly those which are less basic for steric reasons, the use of a strong standard base such as triethylamine gives better results.

The dimethylamino derivative (**3**) was best prepared from **1** and *N*,*N*-dimethylaminotrimethylsilane because the reactions are cleaner and this reagent is more easily handled than dimethylamine. Treating **2** with *N*,*N*-dimethylaminotrimethylsilane was attempted as an alternate route to **3**; however, no reaction occurred under reasonable conditions even though formation of the aminophosphinodiazaphosphole and trimethylfluorosilane should be favored by at least 20 kJ mol^{-1}. The reason for the lack of reaction here is not clear as examples are known in which the reaction proceeds as expected.[25−27] Cases are also known where a fluorophosphorus compound does not react with aminosilanes,[27] and we surmise that the reduced basicity of the fluorinated phosphine **2** may inhibit reaction through kinetic constraints.



1 **3** (4)

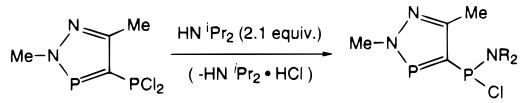


1

4, R = NEt_2
5, R = NPr_2 (5)

The diethylamino (**4**) and di(*n*-propyl)amino (**5**) compounds were prepared following eq 5. In the first case, excess diethylamine worked well as the salt former, but the more basic triethylamine worked better in the reaction of di(*n*-propyl)amine. In this phospholephosphine system the sequestration of HCl is especially important because of the possibility of nucleophilic attack by the evolved acid at the two-coordinate phosphorus center. This was observed in the case of the reaction of trichlorophosphine sulfide with the diazaphosphole.[4] Ideally also the resulting amine salt should be insoluble in the diethyl ether solvent, as in this case, so that it may be easily removed by filtration. These reactions were generally started at 0 °C, and then the solution was allowed to warm to room temperature and maintained with thorough stirring at this temperature for a period of 12 h to ensure complete reaction. Yields were good (70−85%). The simpler diaminophosphinodiazaphosphole derivatives are liquids with colors ranging from light yellow (**3**) to orange yellow (**5**).

The bulkier amines di(isopropyl)amine, dibenzylamine, and iminodibenzyl replaced only one of the chloride atoms of **1** to form asymmetric amino(chloro)phosphinodiazaphospholes **6**, **7**, and **8** (e.g. as in eq 6).



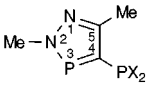
1

6, NR_2 = N^iPr_2
7, NR_2 = $N(CH_2Ph)_2$
8, NR_2 = iminodibenzyl (6)

These results imply substantial steric interaction between the amino group and the diazaphosphole ring and suggest that the largest amines which can be accommodated on the exocyclic phosphine of this phosphine phosphole are *n*-butyl and isopropyl. The reaction between dichlorophosphinophosphole **1** and the more bulky and less basic iminodibenzyl proceeded only in the presence of the much stronger base DBU and produced **8**

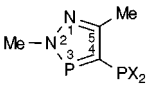
(21) Friebolin, H., *Basic One- and Two-Dimensional NMR Spectroscopy*; VCH Publishers, New York, NY, 1991; pp 150−153.
(22) Verkade, J. G.; Mosbo, J. A., In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Ed.; VCH Publishers, Inc.: Deerfield Beach, FL, 1987; Vol. 8, pp 425−463.
(23) Henderson, J., W.A.; Buckler, S. *A. J. Am. Chem. Soc.* **1960**, *82*, 5794−5800.
(24) Cavell, R. G. Unpublished results, University of Alberta, Edmonton, Alberta, Canada.
(25) Grapov, A. F.; Mel'nikov, N. N.; Razvodovskaya, L. V. *Russ. Chem. Rev.* **1979**, *39*, 20.
(26) Murray, M.; Schmutzler, R. *Z. Chem.* **1968**, *8*, 241.
(27) Schmutzler, R. *Halogen Chem.* **1967**, *2*, 55.

Table 1. Principal Infrared Data for 4-(Phosphino)-2,5-dimethyl-2*H*-1,2,3σ^2-diazaphospholes



X	R	no.	IR bands (cm^{-1})	
			ν(P−F)	
F		**2**	805, 780	
			ν(P−N)	ν(N−C)
NR_2	Me	**3**	713, 656	969, 950
	Et	**4**	717, 663	1013, 967
	^{n}Pr	**5**	716, 557	1019, 971
Cl (X^1),	^{i}Pr	**6**	692	1055
NR_2 (X^2)	CH_2Ph	**7**	680	985
	iminodibenzyl	**8**	672	962
R	pyrazole	**9**	721	994
	1,3-dimethylpyrazole	**10**	714	982
			ν(P−O)	
OR	CH_2CF_3	**11**	1175	
	Ph	**12**	1226	
	C_6F_5	**13**	1195	
	2,6-$F_2C_6H_3$	**14**	1187	
	$CH_2C_6F_5$	**15**	1182	

Table 2. Principal $^{31}P\{^1H\}$ NMR Data for 4-(Phosphino)-2,5-dimethyl-2*H*-1,2,3σ^2-diazaphospholes[a,b]



X	R	no.	$\delta\ \sigma^2$P (ppm)	$\delta\ \sigma^3$P (ppm)	$^2J_{PP}$ (Hz)
Cl		**1**	248.51[c]	154.14[c]	79
F		**2**	255.03[d,e]	208.84[d,e]	107
NR_2	Me	**3**	243.23[c]	86.88[c]	33
	Et	**4**	242.54[c]	77.94[c]	29
	^{n}Pr	**5**	241.53[c]	78.99[c]	23
Cl (X^1),	^{i}Pr	**6**	248.53[c]	120.40[c]	29
NR_2 (X^2)	CH_2Ph	**7**	247.43[c]	127.48[c]	25
	iminodibenzyl	**8**	246.51[c]	118.46[c]	6
R	pyrazole	**9**	243.84[c]	59.19[c]	7
	1,3-dimethylpyrazole	**10**	242.84[c]	49.28[c]	4
OR	CH_2CF_3	**11**	247.27[c]	168.09[f,g]	25
	Ph	**12**	247.00[c]	158.13[c]	36
	C_6F_5	**13**	248.49[c]	188.89[h,i]	57
	2,6-$F_2C_6H_3$	**14**	247.76[c]	167.54[h,j]	39
	$CH_2C_6F_5$	**15**	246.09[c]	161.04[h,k]	23

[a] Chemical shifts δ in ppm with respect to 85% H_3PO_4. Positive shifts lie to low field of the standard. [b] In $CDCl_3$ solution. [c] Doublet. [d] Doublet of triplets. [e] Fluorine couplings: $^1J_{PF} = 1169$ Hz; $^3J_{PF} = 34$ Hz. [f] Doublet of quartets. [g] $^4J_{PF} = 4$ Hz. [h] Doublet of pentets. [i] $^4J_{PF} = 29$ Hz. [j] $^4J_{PF} = 27$ Hz. [k] $^5J_{PF} = 6$ Hz.

with a relatively poor yield (33%). Surprisingly, however, pyrazole and 2,5-dimethylpyrazole reactions proceeded smoothly with normal bases as the salt formers and gave the disubstituted derivatives **9** and **10** in good yield presumably because the planar rings can be appropriately oriented. Both pyrazole derivatives were extremely moisture sensitive white solids, the 3,5-dimethylpyrazole being slightly less reactive toward moisture.

Detailed NMR data for the 4-(amino(chloro)phosphino)-diazaphospholes are given in Tables 2−4 and in the Supporting Information. As the NMR chemical shift value of a phosphine (except for a fluorophosphine) can be estimated from a sum of contributions from each of the substituents on the phosphorus center, we can evaluate the number of amino groups attached to the exo phosphorus atom by comparing the $^{31}P\{^1H\}$ NMR shift values for the aminophosphines to the phosphorus shift value for **1**. Thus phosphorus chemical shifts for the disubstituted aminophosphines (77.9 ppm for **4** and 86.9 ppm for **3**) lie much further downfield than the value for **1** whereas the monosubstituted derivatives **7** and **8** lie in between, strongly suggesting that only partial substitution had occurred. This was confirmed with mass spectrometry and elemental analysis. In accord with this property, the ^{31}P NMR shifts for both pyrazole type derivatives (**9** and **10**) were highly shifted downfield vs **1**, confirming that complete substitution had occurred.

In contrast to **2**, wherein $^2J_{PP}$ increased vs the value for **1**, these coupling constants in the diamino derivatives decreased significantly and the decline through the sequence **3** to **4** to **5** correlates with increasing chain length of the alkyl group on nitrogen. The corresponding aminochlorophosphines **6** and **7** showed a similar trend for $^2J_{PP}$ values. The iminodibenzyl derivative had a very low $^2J_{PP}$ value (6 Hz), as did the pyrazolephosphines, **9** and **10**.

The $^{13}C\{^1H\}$ NMR spectra of the aminophosphinephospholes **3**−**10** (Table 4) showed shift and coupling parameters for the C^4 and C^5 carbon centers similar to those of the other derivatives of **1** with perhaps the exception of the pyrazole derivatives **9** and **10**. In general the C^5 ring carbon is coupled to both the σ^2P and the σ^3P centers ($^2J_{\sigma^2PC}$ about 7 Hz, $^2J_{\sigma^3PC}$ about 19−25 Hz). The ^{13}C carbon at the 4-position showed coupling to both phosphorus atoms ($^1J_{\sigma^2PC}$ about 55 Hz, $^1J_{\sigma^3PC}$ about 9 Hz). In all cases the ring carbon at the 2-position and the pendant methyl group at the 5-position are coupled only to the σ^2P center, the latter being notably large (∼17 Hz). The carbon signal for the dimethylamino group of compound **3** (40.7 ppm) was a singlet. For **4**, the methylene carbons of the ethylamino group (42.5 ppm) were coupled to the σ^3P center ($^2J_{\sigma^3PC}$ 17 Hz) while the methyl groups were singlets (14.5 ppm).

The ^1H NMR spectra also showed significant couplings to the phosphorus centers; thus the protons for the 2-methyl groups were coupled to the σ^2P center (∼7 Hz), but the protons of the 5-methyl group appeared as singlets. The dimethylamino protons of **3** showed coupling to the σ^3P center (9.5 Hz), but this carbon atom was not similarly coupled, vide supra. The splitting pattern for the methylene protons in the diethylamino derivative (**4**), a doublet of quartets, is due to coupling of these protons both with the σ^3P center and to the methyl protons ($^3J_{\sigma^3PH}$ 9.8 Hz, $^3J_{HH}$ 6.9 Hz). The methyl protons (1.00 ppm) appeared as triplets, showing coupling only to the methylene protons ($^3J_{HH}$ 6.9 Hz). The *N*-methylene proton signal for the dipropylamino derivative (**5**) was a doublet of triplets (3.02 ppm, $^3J_{\sigma^3PH}$ 9.6 Hz, $^3J_{HH}$ 7.0 Hz) while the signals for the remaining protons for the propyl group appeared as complex multiplets containing considerable coupling interaction, which was not resolved.

When only one of the Cl atoms on the exo-phosphorus center is replaced (e.g., **6**) the σ^3P unit becomes stereogenic and inequivalent and magnetically anisochronous methyl groups are developed on the isopropyl substituent, a feature often observed in phosphines with isopropyl substituents.[28] In our system, only the methine protons showed a coupling to the phosphorus center (σ^3P). Broadened $^{13}C\{^1H\}$ and ^1H NMR signals for **6** indicated that the isopropyl group environments were subject to fluxional averaging at room temperature (Figures 3 and 4), which is presumably due to bond rotational processes typical of phosphine systems. Under the same conditions the methyl groups

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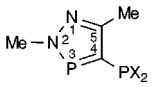
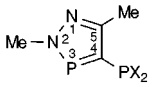
Table 3. Principal ^{1}H NMR Data for Diazaphosphole Protons in 4-(Phosphino)-2,5-dimethyl-2*H*-1,2,3σ^2-diazaphospholes[a,b]



X	R	no.	δ CH_3−N (ppm)	$^3J_{\sigma^2PH}$ (Hz)	δ C−CH_3 (ppm)	$^2J_{PH}$ (Hz)
Cl		**1**	4.03[c]	8	2.51[c]	2.1
F		**2**	4.00[d]	10.7	2.50	
NR_2	Me	**3**	3.80[c]	7.2	2.10	
	Et	**4**	3.90[c]	6.8	2.27	
	^{n}Pr	**5**	3.93[c]	6.8	2.28	
Cl (X^1), NR_2 (X^2)	^{i}Pr	**6**	3.90[c]	7.8	2.31	
	CH_2Ph	**7**	4.03[c]	7.6	2.44[d]	1.8
	iminodibenzyl	**8**	3.98[c]	7.8	2.40[d]	1.5
R	pyrazole	**9**	4.04[d]	7.7	2.38[d]	1.6
	1,3-dimethylpyrazole	**10**	4.02[d]	7.5	2.26[d]	1.7
OR	CH_2CF_3	**11**	4.02[c]	7.9	2.48[c]	0.8
	Ph	**12**	4.09[c]	8.1	2.51	nr[e]
	C_6F_5	**13**	4.13[c]	7.8	2.65	nr[e]
	$CH_2C_6F_5$	**15**	4.04[c]	7.9	2.45[c]	0.8

[a] Chemical shifts δ in ppm with respect to $SiMe_4$. [b] In $CDCl_3$. [c] Doublet. [d] Doublet of doublets. [e] Not resolved.

Table 4. Principal ^{13}C{^{1}H} NMR Data for Diazaphosphole Carbons in 4-(Phosphino)-2,5-dimethyl-2*H*-1,2,3σ^2-diazaphospholes[a,b]



X	R	no.	$^2J_{\sigma^2PC}$ (Hz)	δ C^4 (ppm)	$^1J_{\sigma^2PC}$ (Hz)	$^1J_{\sigma^3PC}$ (Hz)	δ C^5 (ppm)
Cl		**1**	57	150.21[d]	63	49	156.20[d]
F	F	**2**	19	135.17[d]	35	6	157.21[d]
NR_2	Me	**3**	17	150.95[d]	54	9	155.68[d]
	Et	**4**	17	153.16[d]	55	9	155.54[d]
	Pr	**5**	17	152.69[d]	55	9	156.05[d]
Cl (X^1), NR_2 (X^2)	^{i}Pr	**6**	18	148.86[d]	51	32	153.98[d]
	CH_2Ph	**7**	18	150.73[d]	54	36	155.38[d]
	iminodibenzyl	**8**	17	151.07[d]	53	35	155.52[d]
R	pyrazole	**9**	18	135.77[c]	18	n.o.[e]	144.63[d]
	3,5-dimethylpyrazole	**10**	18	136.27[c]	18	n.o.[e]	145.53[d]
OR	CH_2CF_3	**11**	18	146.44[d]	59	29	156.73[d]
	Ph	**12**	18	147.25[d]	57	27	156.56[d]
	C_6F_5	**13**	18	146.68[d]	56	27	157.76[d]
	$CH_2C_6F_5$	**15**	18	148.02[d]	58	28	156.52[d]

[a] Chemical shifts δ in ppm with respect to $SiMe_4$. [b] In $CDCl_3$. [c] Doublet. [d] Doublet of doublets. [e] Not observed.

on the phosphole ring gave sharp signals. Cooling the sample to 0 °C resulted in a sharpening of all isopropyl group ^{13}C signals to reveal two different methine carbon signals at 49.1 ppm ($^2J_{\sigma^3PC}$ 12 Hz) and 45.4 ppm ($^2J_{\sigma^3PC}$ 26 Hz) as expected. For one of the isopropyl groups the resonances for two methyl carbon atoms were similar and only one of the carbon signals was coupled to the σ^3P center (21.4 ppm, $^4J_{\sigma^3PC}$ 3 Hz; 21.1 ppm). In the second isopropyl group, both of the signals arising from the two methyl carbon atoms showed coupling to the σ^3P center but of different magnitude ($^4J_{\sigma^3PC}$ 5 Hz, 24 Hz). The phosphole ring carbon signals of **6** as well as those in the 2- and 5-methyl groups showed sharp signals at room temperature in the ^{13}C-{^{1}H} NMR spectrum with appropriate coupling constants revealed. The ^{13}C NMR spectrum of the isopropyl group region at room temperature showed a broad pattern of methine signals (49.4 and 46.1 ppm) and also three methyl group peaks (25.6, 23.8, and 21.7 ppm) consistent with the chemical inequivalence within the anisochronous isopropyl group.

In the ^{1}H NMRspectrum of **6** at 0 °C, the methine proton resonances remained broad and unresolved but two distinct proton environments (3.79 and 3.44 ppm) were observed for the methyl group signals. The methyl groups of the isopropyl group showed four distinct proton resonances (1.38, 1.29, 1.09, and 0.80 ppm) at this temperature. At −25 °C, the peaks in the isopropyl region of the ^{1}H NMR spectrum sharpened to reveal two distinct methine proton resonances centered at 3.76 ppm

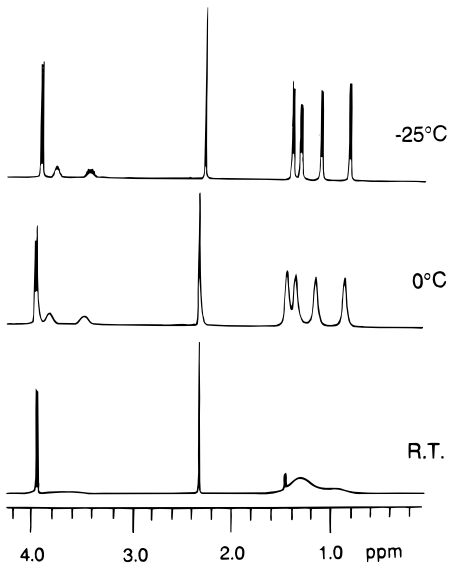


Figure 3. ^{1}H NMR spectra of compound **6** in $CDCl_3$ at −25 °C, 0 °C, and normal probe temperature (~33 °C).

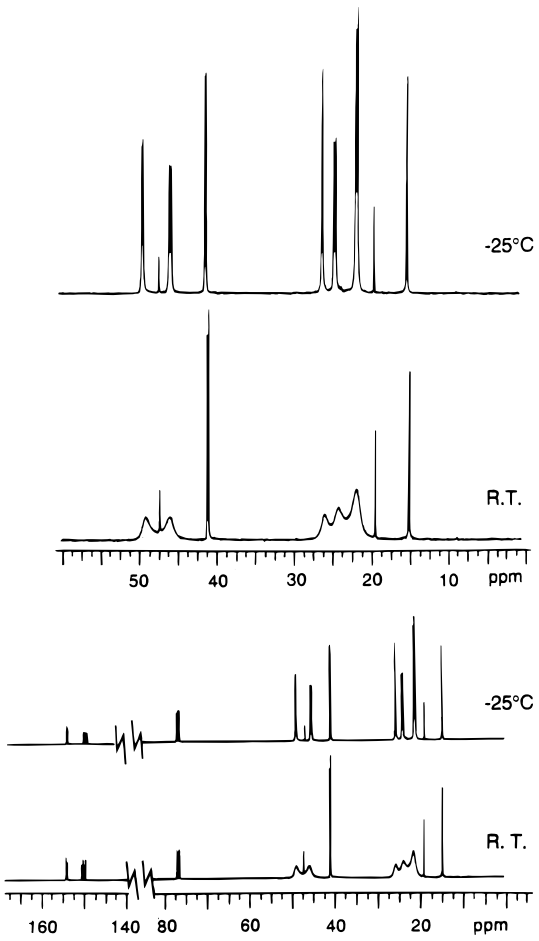


Figure 4. Methyl region $^{13}C\{^1H\}$ NMR spectra of compound **6** at −25 °C and normal probe temperature (∼33 °C) in $CDCl_3$. The upper spectrum shows the expanded methyl region spectra at the same temperatures.

(doublet of septets, $^3J_{\sigma^3PH}$ 9.9 Hz; $^3J_{HH}$ 6.7 Hz) and at 3.42 ppm (doublet of septets, $^3J_{\sigma^3PH}$ 17.7 Hz; doublet, $^3J_{HH}$ 6.7 Hz). Four resonances for the methyl group signals were observed at 1.36 ppm (doublet, $^3J_{HH}$ 6.7 Hz), 1.28 ppm (doublet, $^3J_{HH}$ 6.7 Hz), 1.07 ppm (doublet, $^3J_{HH}$ 6.7 Hz), and 0.78 ppm (doublet, $^3J_{HH}$ 6.7 Hz). Decoupling experiments showed that the methine protons at 3.76 ppm were coupled to the methyl protons at 1.36 ppm and at 1.26 ppm whereas the methine protons at 3.42 ppm were coupled to the other two methyl protons at 1.07 ppm and at 0.78 ppm; thus a full assignment could be made. Furthermore, a two-dimensional C,H-correlation (HETCOR) NMR spectrum of **6** (Figure 5) showed that the two equivalent carbons at 21.2 ppm correlated to the methyl protons at 1.07 ppm and 0.78 ppm. The methyl protons at 1.36 ppm correlated to the carbon at 24.2 ppm, while the methyl protons at 1.28 ppm correlated to the carbon at 25.7 ppm. The methine proton at 3.75 ppm correlated to the carbons at 49.2 ppm, and the methine proton at 3.41 ppm correlated to the carbon at 45.2 ppm. The protons on the carbons resonating at the higher fields may be influenced by ring currents of the aromatic five-membered ring system, which may account for the shift in these signals.

The chloro(dibenzylamino)phosphino analogue (**7**) showed very similar spectral behavior in that the methylene carbons of the benzyl groups were diastereotopic and fluxional at ordinary temperatures. Resolution of the environments at −30 °C showed sharpened peaks with additional coupling to phosphorus. The larger $^2J_{PC}$ coupling (39 Hz) was associated with the resonance at 54.5 ppm, and the smaller (14 Hz) was associated with the

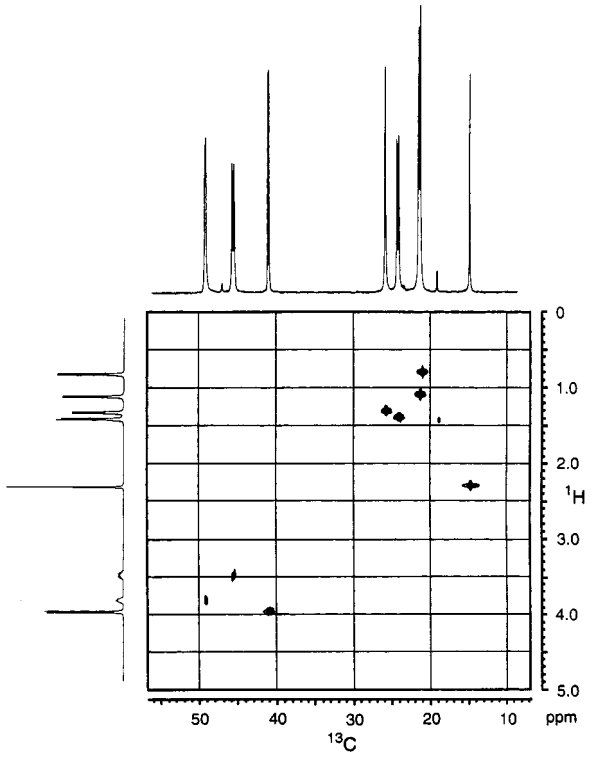
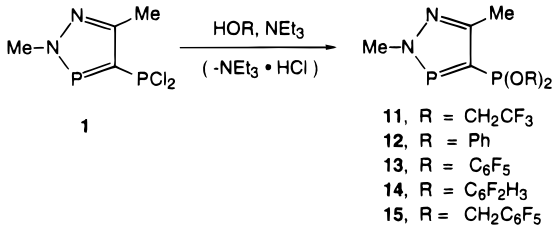


Figure 5. Two-dimensional C,H-correlation (HETCOR) spectrum for compound **6** at −20 °C in $CDCl_3$. The ^{13}C spectrum is displayed on the horizontal axis, the ^1H spectrum on the vertical axis.

resonance at 48.2 ppm. The phosphole carbon signals were sharp peaks at normal temperature and revealed notable couplings to both phosphorus centers, with a wide variation in values (Table 4). Notably the signal for the *ipso*-carbon on the phenyl ring (136.4 ppm) also showed a coupling to the phosphorus ($^2J_{\sigma^3PC}$ 3 Hz). The methylene protons signals in the ^1H NMR spectrum of **7** showed diastereotopic character but were not fluxional at room temperature, in contrast to the behavior revealed by the ^{13}C spectra. The methylene group resonating at 4.12 ppm gave the appearance of a triplet because $^3J_{\sigma^3PH}$ was similar to the geminal $^2J_{HH}$ (15 Hz) coupling. The methylene proton signal at 4.30 ppm showed a smaller $^3J_{\sigma^3PH}$ (9.5 Hz) to give a doublet of doublets splitting pattern. The proton resonance for the 2-methyl group (4.03 ppm) showed coupling to the σ^2P center ($^3J_{PH}$ 7.6 Hz), but the 4-methyl group protons (2.44 ppm) did not show any phosphorus−proton coupling. Neither the $^{13}C\{^1H\}$ nor the ^1H NMR spectra for **8** showed any evidence of fluxionality.

3. Alkoxy- and Aryloxyphosphine Diazaphospholes. Five alkoxy phosphinodiazaphosphole (**11**−**15**) derivatives were synthesized in good yield using a procedure similar to that described for the diethylaminophosphinophospholes. In all cases, triethylamine was used as the base (eq 7) to remove hydrogen chloride, to suppress nucleophilic reactions on the phosphole ring, and also to supress the Arbuzov rearrangement, although all the alcohols chosen contained electron-withdrawing fluorine atoms (e.g., a CF_3 group) or a phenyl ring and the Arbuzov reaction is not expected to be important.

All compounds (Table 1) show ν(P−O) frequencies between 1230 and 1184 cm^{-1}, well within the typical range for the phosphorus−oxygen single bond stretching frequencies characteristic of alkyl (1190−1170 cm^{-1}) or aryl (1240−1190 cm^{-1}) phosphites.[19] The NMR data (Tables 2−4) show σ^3P phosphorus chemical shift values which are very similar to those of the parent phosphinodiazaphosphole **1**; thus the aryl- or alkoxide substituents do not alter the electronic environment of the



1

11, R = CH_2CF_3
12, R = Ph
13, R = C_6F_5
14, R = $C_6F_2H_3$
15, R = $CH_2C_6F_5$ (7)

phosphine. The only exception was the pentafluorophenoxy derivative **13** (188.9 ppm), which was highly shifted downfield (closer to the difluoro analogue) presumably because of the highly enhanced electron-withdrawing ability of this fully fluorinated aromatic group. In all cases the σ^2P shifts also varied little from that of **1**. The $^2J_{PP}$ values for these compounds were in general smaller (25−57 Hz) than those for **1**. In all cases, coupling of any fluorine atoms present to the σ^3P center was observed, although those compounds which contain fluoroaromatic substituents showed coupling of only the fluorines in the ortho position of the aromatic ring to the σ^3P center. The coupling constants extracted ranged from 6 to 29 Hz and correlated with the number of intervening atoms.

The $^{13}C\{^1H\}$ NMR chemical shifts of the carbon signals at the 4-position of **11**−**13** and **15** were relatively unchanged thoughout the series at approximately 147 ppm. These signals showed coupling to both phosphorus centers (typically $^1J_{\sigma^2PC}$ values of 56−59 Hz and $^1J_{\sigma^3PC}$ values of 27−29 Hz). The carbon at the 5-position of the ring also showed little variation in chemical shift position (close to 157 ppm), and again this carbon was coupled to both phosphorus atoms with small $^1J_{\sigma^2PC}$ (4−6 Hz) and $^1J_{\sigma^3PC}$ (23−24 Hz) values. The phenyl carbon shifts were between 135 and 145 ppm except for the ipso carbons of **13** (129.2 ppm) and **15** (111.3 ppm). The general range of $^1J_{CF}$ values was 210−250 Hz, and $^2J_{CF}$ was usually not resolved; however, for **11**, with a larger $^1J_{CF}$ value (278 Hz), $^2J_{CF}$ was 7 Hz.

The fluorine NMR spectrum for **11** gave a resonance centered at −75.7 ppm which showed a splitting pattern of a doublet of doublet of triplets due to coupling of ^{19}F to both phosphorus centers ($^6J_{\sigma^2PF}$ 2.2 Hz and $^4J_{\sigma^3PF}$ 3.5 Hz) and to the two methylene protons (8.4 Hz). Characteristic chemical shifts for the various ring position signals *o*- (−162.2 ppm), *m*- (−154.7 ppm) and *p*-fluorine (−161.2 ppm) of **13** were observed, but because all the fluorine resonances of **13** were second order, it was not possible to obtain the fluorine−fluorine coupling constants. Chemical shifts for the *o*-fluorines of **15** occurred at −162.6 ppm ($^3J_{FF}$ 22 Hz, $^4J_{\sigma^3PF}$ 13 Hz), while the *m*-fluorines resonated at −143.3 ppm and the *p*-fluorine at −153.5 ppm ($^3J_{FF}$ 21 Hz) and fluorine−fluorine coupling constants were partially resolved.

The ^1H NMR spectrum for **11** and **15** showed a 2-methyl group ring signal (ca. 4.0 ppm) which was coupled only to the σ^2P center (7.9 Hz). The signal for the protons for the 5-methyl group (ca. 2.45 ppm) was coupled to both phosphorus centers with the same value for the coupling constant ($^4J_{PH}$ 0.8 Hz). Two signals were observed for the methylene protons (4.21 and 4.06 ppm). Compounds **12** and **13**, however, showed the 2-methyl group resonance (ca. 4.1 ppm) to be observably coupled to the σ^2P center (ca. 8 Hz), but the 5-methyl groups (at ca. 2.5−2.6 ppm) were singlets. Both **11** and **15** showed two signals for the methylene group protons (4.93 and 4.83 ppm) because of their diastereotopic character arising from the different relative positions of each proton with respect to the ring in the molecule. In the case of **11**, decoupling the phosphorus affected only one proton resonance, that at δ 4.06, which has a coupling to the σ^3P center of 0.4 Hz. For **15**, the chemical shifts for the methylene protons were broadened due to proton−fluorine coupling and the coupling was not clearly resolved.

4. Complexation Reactions of 2. The coordination chemistry of the 4-(difluorophosphino)-2,5-dimethyl-2*H*-1,2,3σ^2-diazaphosphole (**2**) showed, in all cases, coordination of the metal center with only the exo-phosphorus center. The chemistry of the difluorophosphine ligand is similar to that of phosphites and phosphorus trifluoride which can be attributed to the electron-withdrawing power of the fluorine substituents on the exo-phosphorus center. Thus 1 equiv of **2** reacted with $Cr(CO)_5$-(THF), generated in situ from the photolysis of $Cr(CO)_6$ in THF, to form $Cr(CO)_5$(**2**) (**16**) as bright yellow crystals in good yield (72%). Complex **16** has a low melting point (64 °C) similar to that of $Cr(CO)_5(PF_3)$.[29]

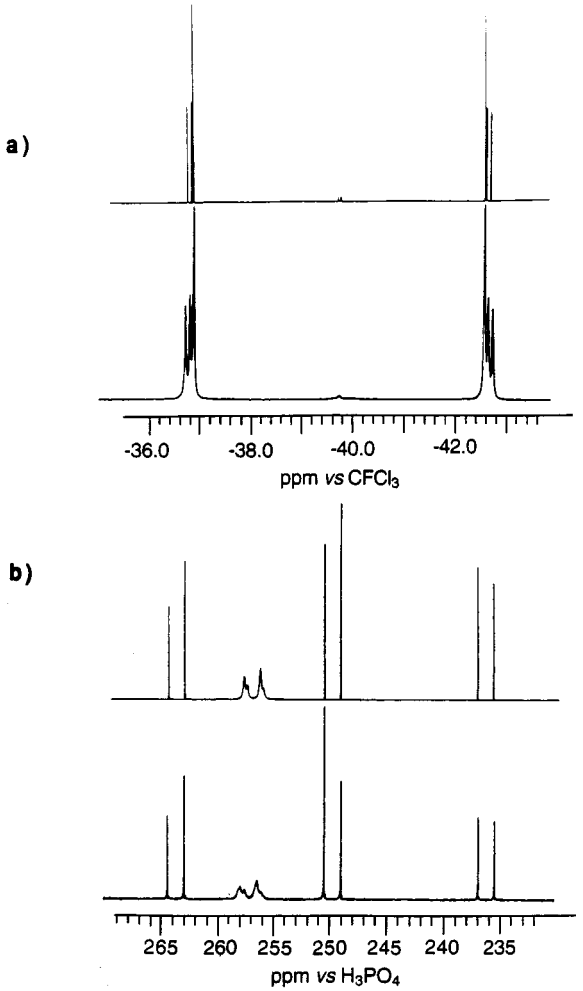


Figure 6. (a) ^{19}F NMR spectrum at (188.313 MHz) and (b) $^{31}P\{^1H\}$ spectrum (at 81.015 MHz) of **16** in $CDCl_3$ at room temperature. Simulations[15] are displayed above the experimental spectra.

The $^{31}P\{^1H\}$ NMR spectra of the complexes (Figures 6 and 7) were second order. Relative to the free ligand, there was a large downfield shift for the resonance of the exo-phosphorus center of the order of 45 ppm accompanied by only a small downfield shift of 2 ppm for the σ^2P signal, with the result that the two signals overlap strongly. Further complications arise because of the contribution of a large $^1J_{PF}$ value. The $^2J_{PP}$ value

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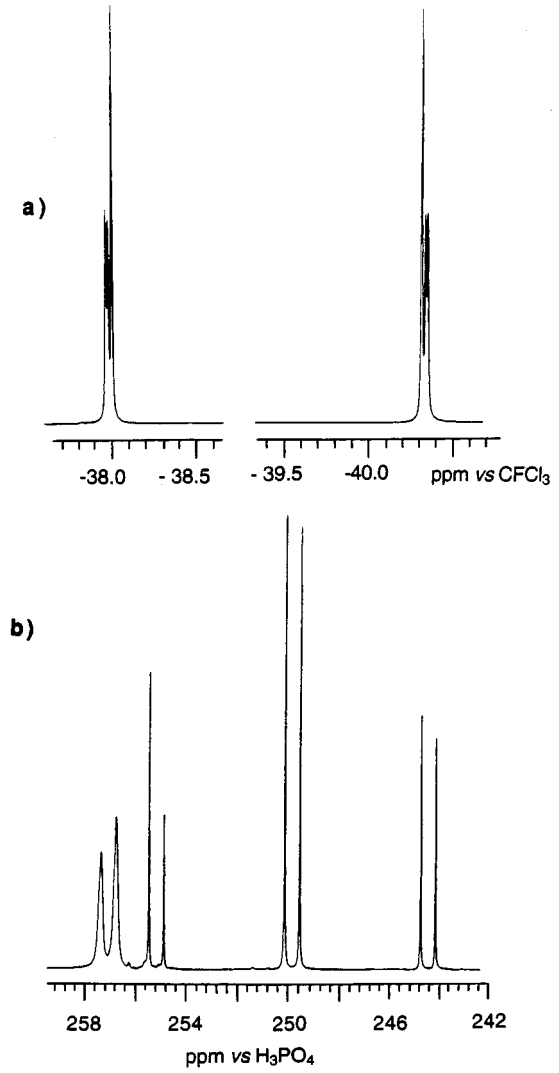

Figure 7. (a) ^{19}F NMR spectrum (at 470.304 MHz) and (b) ^{31}P{^{1}H} spectrum (at 202.392 MHz) of **16** in $CDCl_3$ at room temperature.

extracted from these spectra is of the order of 120 Hz, substantially greater than that of the free ligand, while the value $^{1}J_{PF}$ was approximately 1140 Hz. Thus in the ^{31}P{^{1}H} NMR spectrum of **16** at 81.013 MHz the two phosphorus signals are overlapped and the peak for the σ^2P endo phosphorus is skewed and broadened (Figure 6). At 161.977 MHz, the σ^2P signal merged with one component of the σ^4P signal, so a second-order ^{31}P{^{1}H} NMR spectrum is again observed (Figure 7). At all frequencies, the ^{19}F NMR spectra were also second order (Figures 6 and 7). Simulation with gNMR[15] gave values of $^{1}J_{PF}$ 1150 Hz, $^{2}J_{PP}$ 120.0 Hz, and $^{3}J_{PF}$ (−)10.0 Hz for **16**.

The IR spectrum of **16** showed the two stretching frequencies for the carbonyls at ν(CO) 2079 cm^{-1} and at ν(CO) 1938 cm^{-1} (Table 5). We can estimate the basicity or the π acidity of **2** from a comparison of the A_1 stretching band of (**16**) with those of related phosphine and phosphite complexes of chromium pentacarbonyl, which indicates that the basicity of **2** was greater than that of PF_3 (2083 cm^{-1}), similar to that of the caged phosphite $P(OCH_2)_3CMe$ (2082 cm^{-1}), but was less basic than $P(OMe)_3$ (2073 cm^{-1}). Unfortunately similar carbonyl stretching frequencies were not reported for the analogous dichlorophosphinodiazaphosphole or dimethoxyphosphinodiazaphosphole complexes[30] and so a full and direct comparison with these previously reported chromium complexes cannot be made at this time. Following Tolman[31] we estimate the electronic parameter χ for the phosphine **2** by estimating the stretching frequencies of the nickel complexes $LNi(CO)_3$ from the values observed for the chromium analogues $Cr(CO)_5L$. The resultant value χ for **2**, 51 cm^{-1}, is comparable to that for PF_3 (χ = 55 cm^{-1}).

Table 5. Carbonyl Infrared Stretching Frequencies for Complexes

complex	ν(CO) (cm^{-1})	ref
$Cr(CO)_5L$		
16	2079	this work
$Cr(CO)_5(PF_3)$	2083	29
$Cr(CO)_5(P(OCH_2)_3CMe)$	2082	32
$Cr(CO)_5(P(OMe)_3)$	2073	33
$Cr(CO)_5(P(C_4H_9)_3)$	2062	34
$Cr(CO)_5(P(NMe_2)_3)$	2055	35
cis-$Mo(CO)_4L_2$		
17	2056, 1974, 1952[a]	this work
$Mo(CO)_4(PF_3)_2$	2091, 2022, 2003[a]	36
$Mo(CO)_4(P(OCH_2)_3CMe)_2$	2045, 1965, 1945[a]	37
$Mo(CO)_4(P(OMe)_3)_2$	2037, 1945, 1926, 1921	33
$Mo(CO)_4(PMe_3)_2$	2024, 1930, 1901, 1879	38
$Mo(CO)_4(P(NMe_2)_3)_2$	2012, 1908, 1894, 1880	39
fac-$Mo(CO)_3L_3$		
18	2011, 1945	40
$Mo(CO)_3(PF_3)_3$	2090, 2055	40
$Mo(CO)_3(PCl_3)_3$	2040, 1991	40
$Mo(CO)_3(P(OMe)_3)_3$	1977, 1888	40
$Mo(CO)_3(PPh_3)_3$	1934, 1835	40
$Mo(CO)_3(MeCN)_3$	1915, 1783	40

[a] B_1 and B_2 bands were unresolved.

When **2** was added to a solution of $Mo(CO)_5$(THF), the color of the solution slowly bleached and a brown precipitate formed; however we were not able to recover an identifiable product. Similarly, addition of **2** to a solution of $W(CO)_5$(THF) gave a grayish purple solid which, according to the ^{31}P{^{1}H} NMR spectrum, was a mixture of products which could not be characterized. Reacting 2 equiv of **2** with $Mo(CO)_4$(nbd) (eq 8), however, gave a clean (74%) yield of *cis*-$Mo(CO)_4$(**2**)$_2$ (**17**).

The ^{31}P{^{1}H} NMR spectrum of **17** consisted of an AA′BB′-$X_2X'_2$ spin system, typical of that usually observed with disubstituted phosphine metal complexes as the result of the proximity of the σ^2P (259.74 ppm) and σ^3P (222.99 ppm) due to the substantial shift of the coordinated phosphine which occurs on complexation. The ^{19}F NMR spectrum is also second order with the signals centred at −42.91 ppm. The major coupling constants obtained by simulation[15] were $^{1}J_{PF}$ 1160 Hz, $^{3}J_{PF}$ 15.0 Hz, $^{2}J_{PP}$ 146.0 Hz, and $^{3}J_{PMP'}$ 33.0 Hz.

The carbonyl region ^{13}C{^{1}H} NMR spectrum of **17** showed two weak signals; one of the peaks (208.32 ppm) was a doublet due to coupling to the trans phosphorus center (39 Hz) while the other signal (212.35 ppm) was a singlet. The proton

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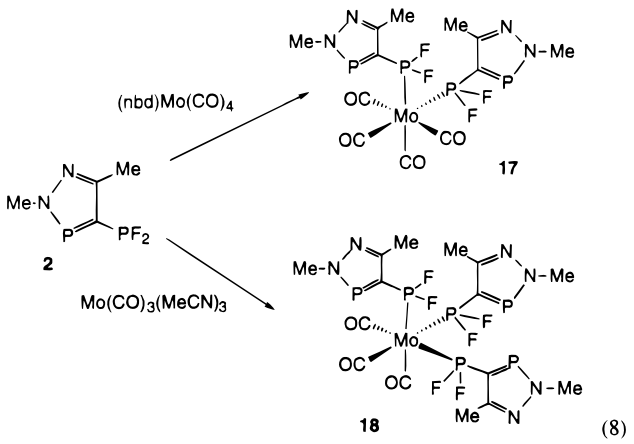

(8)

resonances did not change significantly with respect to the uncomplexed ligand.

The carbonyl region infrared spectrum of **17** showed three peaks at 2056, 1974, and 1952 cm^{-1} consistent with a cis structure in which the B_1 and B_2 bands are unresolved. A comparison with related *cis*-$Mo(CO)_4(PR_3)_2$ complexes is given in Table 5.

Reaction of $Mo(CO)_3(MeCN)_3$ with 3 equiv of **2** (eq 8) appeared to result in complete replacement of the coordinated acetonitrile as no coordinated acetonitrile signals remained in the ^1H NMR spectrum. Both phosphorus signals were second order in the $^{31}P\{^1H\}$ 27 NMR spectrum. The chemical shift for the signal of the two-coordinate phosphorus atom was centered at 257 ppm, not significantly different from that of the disubstituted molybdenum complex **18**, but the signal for the exo-phosphorus center (224.60 ppm) was more complicated. The fluorine peaks in the ^{19}F NMR were broadened due to unresolved coupling. The carbonyl region infrared spectrum of the product was similar to those for related molybdenum L_3 complexes shown in Table 5, showing two peaks consistent with a *fac* structure, but full characterization was not achieved. The results for other systems, reported separately, were more informative; hence the group 6 chemistry was not pursued further.

Conclusions

The dichlorophosphinodiazaphosphole **1** is easily transformed to difluoro-, dialkoxy-, and diaminophosphinodiazaphospholes, in the latter case with the smaller amines (up to *n*-propyl) or pyrazoles. Bulky diamines such as diisopropylamine, dibenzylamine, and iminodibenzyl permit only a single substitution at the exo phosphorus, and as a result asymmetric chloro(aminophosphino)diazaphospholes are obtained. The diastereotopic character of asymmetrically substituted systems such as the chloroaminophosphine (**6**), the chlorodibenzylamino analogue (**7**), and the methylene protons of the 2,2,2-trifluoroethoxy member of the alkoxy series can be observed but usually only in cooled spectra because fluxionality (presumably bond rotation) averages the environments at ordinary temperatures. Throughout the series the two-bond phosphorus−phosphorus coupling constants increased with the increase in electronegativity of the substituent. Substitutions on the exocyclic phosphorus center appear not to impart significant electronic perturbation to the diazaphosphole ring. These new substituted phosphinodiazaphospholes span a range of basicity and steric bulk at the exo-phosphorus center. Limited coordination studies of the fluorinated phosphole show that it is a ligand with good π acceptor properties similar to PF_3 and phosphites. Further studies of the oxidation and complexation chemistry of these phosphinophospholes will be reported in subsequent publications.

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Supporting Information Available: Experimental details for the syntheses of **2**−**15**. This material is available free of charge via the Internet at http://pubs.acs.org.

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