Chemistry of Heterobifunctional Diazaphospholylphosphines. 4. Complexation and Reduction Reactions of Platinum(II) and Palladium(II) with Phosphine-Substituted (Fluoro, Dimethylamino, Trifluoroethoxy) 4-Phosphino-2,5-dimethyl-2*H*-1,2,3σ^2-diazaphospholes. Structure of a Novel Platinum(0) Tetrakis(difluorophosphine) Complex

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Selected platinum(II) and palladium(II) complexes react with 4-(difluorophosphino)-2,5-dimethyl-2*H*-1,2,3σ^2-diazaphosphole (L^F) to form the expected $X_2M(L^F)_2$ complexes. In some cases, redox processes yield stable, solid, $M^0(L^F)_4$ complexes; thus Pd(cod)Cl_2 with L^F gave a mixture of the Pd^0 and Pd^{II} complexes whereas Pt(cod)Cl_2 gave only the $Pt(LF)_2Cl_2$ complex. With limited L^F, (cod)Pt(Me)Cl gave the expected $(L^F)_2$Pt(Me)Cl complex, but when the reaction was carried out with excess L^F, Pt^{II} was reduced to Pt^0 to form the $Pt^0(L^F)_4$ complex. This complex was structurally characterized. Crystal data for $C_{16}H_{28}F_8N_8O_2P_8Pt$: tetragonal, $I\bar{4}2m$ (No. 121), $a = 11.961(2)$ Å, $c = 15.034(3)$ Å, $V = 2150.8(6)$ Å^3, $Z = 2$. Final indices: GOF = 1.299 [$F_o^2 \geq -3\sigma(F_o^2)$] and $R_1 = 0.0381$, w$R_2 = 0.1180$ (for $F_o^2 > 2\sigma(F_o^2)$) and $R_1 = 0.0395$, w$R_2 = 0.1188$ for all data. The structure around the Pt^0 atom was revealed as a slightly squashed tetrahedron surrounded by four phospholylphosphine ligands coordinated through the exocyclic phosphine. The Pt−P distance is 2.237(3) Å. The $Pd(L^F)_4$ analogue was also isolated in pure form from the reaction of L^F with $Pd_2(dba)_3$. The related 4-(bis(dimethylamino))-2,5-dimethyl-2*H*-1,2,3σ^2-diazaphosphole (L^N) displaced cod from M(cod)Cl_2 (M = Pd, Pt) to give only the $(L^N)_2MCl_2$ complexes (M = Pd and Pt) with no evidence for reduction of the metal center. The larger steric bulk of L^N is presumably also the reason this ligand forms the trans complex instead of the cis complexes which were formed by L^F from the same precursors in analogous reactions. The reaction of L^N with (cod)Pt(Me)Cl produced only *cis*-$(L^N)_2$Pt(Me)Cl; there was no evidence of reduction to Pt^0 in contrast to the behavior of L^F. With L^F, the stereochemistry of the final product was the same as that of the starting material. The third ligand, 4-(bis(trifluoroethoxy)phosphino)-2,5-dimethyl-2*H*-1,2,3σ^2-diazaphosphole (L^O) gave the expected platinum cis complex $(L^O)_2MCl_2$ from the (cod)MCl_2 precursor, but palladium rearranged during the complexation reaction to form the trans complex. Again, no evidence for reduction of either Pt or Pd was observed with L^O.

Introduction

We have previously described a set of diazaphospholylphosphine ligands which have been prepared with a variety of substituents on the exocyclic phosphine center,[1] and we have explored the oxidation[2] and some complexation[1,3] chemistry of selected members of the series. These ligands have the advantage of offering both dicoordinate and tricoordinate phosphorus(III) centers so it was of interest to explore the coordination chemistry of this system. The exocyclic phosphine substituents which we can access span a range from the very electronegative fluorine through a variety of amino and alkoxo groups thereby "tuning" both the basicity and the bulk of the phosphine center.[1] Although, at first glance, the diazaphosphole substituent itself appears to possess substantial bulk, we show here Pt(0) or Pd(0) centers can accommodate up to four of the (difluorophosphino)phosphole ligands. Elsewhere, we have also found limited interligand interaction[1−3] so the difluoro ligand does not possess a complexation inhibiting, bulky constitution. Of the two potential phosphorus(III) centers in the ligand, our previous results showed that the exocyclic P(III) was the exclusively preferred coordination site. Some coordination activity at the σ^2 endocyclic site of the simple parent phosphole has previously been demonstrated, particularly toward Pt centers,[4,5] so it was of interest to examine in detail the complexation reactions of some of our phosphinophosphole ligands (Chart 1) with these metals. The literature of phosphine complexes of platinum is extensive,[6] but fluorophosphine[7−9] ligands and phosphole[4,5] ligands have much more limited chemistry.

Experimental Section

All experimental manipulations were performed under an atmosphere of dry argon using standard Schlenk techniques. Deuterated solvents,

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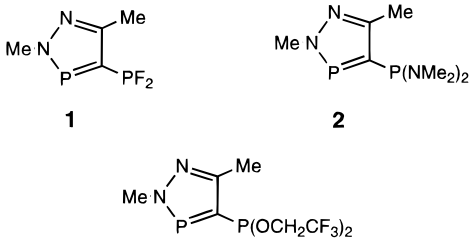
Chart 1. Diazaphospholylphosphine Ligands



$CDCl_3$ and CD_2Cl_2, were distilled over P_4O_{10} 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_4O_{10} and 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, $^{31}P = 81.015$ (Table 1) and 161.977 MHz, and $^{19}F = 188.313$ (Table 1), and 376.503 MHz. External standards for ^{13}C and ^1H were $SiMe_4$ and for ^{31}P 85% H_3PO_4. For ^{19}F, $CFCl_3$ was used as solvent, internal reference, and internal lock. Positive shifts lie downfield in all cases. NMR spectra were simulated using the Brüker software PANIC[10] or gNMR.[11] 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. 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.

The ligands 4-(difluorophosphino)-2,5-dimethyl-2*H*-1,2,3σ^2-diazaphosphole (**1**), 3-(bis(dimethylamino)phosphino)-2,5-dimethyl-2*H*-1,2,3σ^2-diazaphosphole (**2**), and 4-(bis(2,2,2-trifluoroethoxy)phosphino)-2,5-dimethyl-2*H*-1,2,3σ^2-diazaphosphole (**3**) were derived from 4-(dichlorophosphino)-2,5-dimethyl-2*H*-1,2,3σ^2-diazaphosphole[12−14] and prepared as described elsewhere.[1] The metal complexes $Pt(cod)Cl_2$,[15] Pt(cod)(Me)Cl,[16] $Pd(cod)Cl_2$,[17] $Pd_2(dba)_3{\cdot}CHCl_3$,[18] $[Pt(PEt_3)Cl_2]_2$,[19,20] and $[Pd(PEt_3)Cl_2]_2$[21] were prepared according to literature procedures.

Preparations. *cis*-Pt(1)$_2$Cl$_2$ (4). A solution of phosphole **1** (0.10 mL, 0.72 mmol) in 10 mL of dichloromethane was added dropwise at room temperature (22 °C) to a solution of $Pt(cod)Cl_2$ (1.350 g, 0.36 mmol) in 15 mL of dichloromethane and stirred for 4 h. 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 to give **4** as an off-white powder (0.196 g, 86.3%), mp 129 °C (dec). Anal. Calcd for $C_8H_{12}Cl_2F_4N_4P_4Pt$: C, 15.25; H, 1.92; Cl 11.25; N, 8.89. Found: C, 15.11; H, 1.96; Cl 11.50; N, 8.81. MS (FAB, *m*/*z*): 630 (M, 7%). IR data (CH_2Cl_2 cast, cm^{-1}): ν(P−F) 852 (s), 793 (s). NMR data ($CDCl_3$) are as follows. $^{31}P\{^1H\}$: P(σ^2) δ 271.21 (d, $^2J_{PP}$ 158 Hz), P(σ^4) δ 159.29 (dt, Pt sat., $^2J_{PP}$ 158 Hz, $^1J_{\sigma^4PF}$ 1184 Hz, $^1J_{PPt}$ 5064 Hz). 1H: C−C*H*$_3$ δ 2.48 (s), P(σ^2)−N−C*H*$_3$ δ 3.96 (d, $^3J_{\sigma^2PH}$ 8 Hz). $^{13}C\{^1H\}$: C−*C*H$_3$ δ 15.49 (s), P(σ^2)−N−*C*H$_3$ δ 44.92 (d, $^2J_{\sigma^2PC}$ 17 Hz), P−*C*−P δ 148.63 (d, $^1J_{\sigma^2PC}$ 34.7 Hz), N−*C*−CH$_3$ δ 155.01 (s). ^{19}F: δ −39.42 (dd, Pt sat., $^2J_{FPt}$ 190 Hz, $^1J_{\sigma^4PF}$ 1130 Hz, $^3J_{\sigma^2PF}$ 12 Hz).

Mixture of *cis*-Pd(1)$_2$Cl$_2$ (5) and Pd(1)$_4$ (6). A solution of phosphole **1** (0.25 mL, 1.8 mmol) in 10 mL of dichloromethane was added dropwise at room temperature (22 °C) to a solution of $Pd(cod)Cl_2$ (0.257 g, 0.90 mmol) in 15 mL of dichloromethane and stirred for 4 h to give a mixture of two complexes, **5** and **6**. NMR data ($CDCl_3$) are as follows. Pd(II) (**5**): $^{31}P\{^1H\}$ P(σ^2) δ 268.88 (d, $^2J_{PP}$ 158 Hz), P(σ^4) δ 144.33 (dt (broad), $^2J_{PP}$ 158 Hz, $^1J_{\sigma^4PF}$ 1184 Hz); ^{19}F δ −39.42 (d) $^1J_{\sigma^4PF}$ 1184 Hz, $^3J_{\sigma^2PF}$ 15 Hz). Pd(0) (**6**): P(σ^2) δ 257.9 (d, $^2J_{PP}$ 118 Hz), P(σ^4) δ 201.2 (dt (broad), $^2J_{PP}$ 118 Hz, $^1J_{\sigma^4PF}$ ∼1160 Hz); ^{19}F δ −57.57 (dd, broadened, $^2J_{\sigma^2PF}$ 15 Hz, $^1J_{\sigma^4PF}$ ∼ 1160 Hz).

Pure Pd(1)$_4$ (6). To a solution of $Pd_2(dba)_3{\cdot}CHCl_3$ (0.137 g, 0.15 mmol) in 15 mL of dichloromethane was added dropwise a solution of phosphole **1** (0.1 mL, 0.72 mmol) in 10 mL of dichloromethane at room temperature (22 °C) and stirred for 4 h. 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 to give **6** as a maroon powder (0.116 g, 92.7%), mp 115 °C (dec). Anal. Calcd for $C_{16}H_{24}F_8N_8P_8Pd$: C, 23.03; H, 2.90; N, 13.43. Found: C, 23.23; H, 2.95; N, 13.42. MS (FAB, *m*/*z*): 838 (M, 4%). IR data (CH_2Cl_2 cast, cm^{-1}): ν(P−F) 833 (s), 778 (s). NMR data ($CDCl_3$) are as follows. $^{31}P\{^1H\}$: P(σ^2) δ 257.88 (d, $^2J_{PP}$ 118 Hz), P(σ^4) δ 201.2 (dt (broad), $^2J_{PP}$ 118 Hz, $^1J_{\sigma^4PF}$ ∼1160 Hz). ^1H: C−C*H*$_3$ δ 2.48 (s), P(σ^2)−N−C*H*$_3$ δ 3.97 (d, $^3J_{\sigma^2PH}$ 8.0 Hz). $^{13}C\{1H\}$: C−*C*H$_3$ δ 15.46 (s), P(σ^2)−N−*C*H$_3$ δ 44.88 (d, $^2J_{\sigma^2PC}$ 18.6 Hz), P−*C*−P δ 146.96 (d, $^1J_{\sigma^2PC}$ 37 Hz), N−*C*−CH$_3$ δ 155.84 (s). ^{19}F: δ −57.57 (dd, broadened,) $^2J_{\sigma^2PF}$ 15 Hz, $^1J_{\sigma^4PF}$ ∼1160 Hz).

Preparation of Pt(1)$_4$ (9). To a solution of Pt(cod)ClMe (0.127 g, 0.36 mmol) in 15 mL of dichloromethane was added dropwise a solution of phosphole **1** (0.25 mL, 1.8 mmol) in 10 mL of dichloromethane at room temperature (22 °C) and stirred for 4 h. 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 to yield **9** as orange crystals (0.208 g, 62.7% based on Pt), mp 136 °C. Anal. Calcd for $C_{16}H_{24}F_8N_8P_8Pt$: C, 20.81; H, 2.62; N, 12.14. Found: C, 20.65; H, 2.68; N, 12.26. MS (FAB, *m*/*z*): 924 (M + 1, 25%). IR data (CH_2Cl_2 cast, cm^{-1}): ν(P−F) 832 (s), 771 (s). NMR data ($CDCl_3$) are as follows. $^{31}P\{^1H\}$: P(σ^2) δ 267.88 (d, $^2J_{PP}$ 159 Hz), P(σ^4) δ 164.90 (dt (broad), Pt sat., $^2J_{PP}$ nr $^1J_{PF}$ 1130 Hz, $^1J_{PPt}$ 5050 Hz). ^1H: C−C*H*$_3$ δ 2.47 (s), P(σ^2)−N−C*H*$_3$ δ 3.99 (d, $^3J_{\sigma^2PH}$ 8.0 Hz). $^{13}C\{^1H\}$: C−*C*H$_3$ δ 15.49 (s), P(σ^2)−N−*C*H$_3$ δ 44.88 (d, $^2J_{\sigma^2PC}$ 16 Hz), P−*C*−P δ 148.35 (d, $^1J_{\sigma^2PC}$ 30 Hz), N−*C*−CH$_3$ δ 154.23 (s). ^{19}F: δ −46.7 (d, broad, $^1J_{PF}$ 1128 Hz).

When less than 2 equiv of **1** were used in this reaction, the $^{31}P\{^1H\}$ NMR spectrum (Figure 1) showed a signal for one of the Pt coordinated σ^4 phosphorus centers at 135.6 ppm ($^1J_{PPt}$ 6089 Hz) while the other Pt coordinated σ^4 resonance was observed at 186.61 ppm ($^1J_{PPt}$ 2511 Hz). Both signals were readily assigned to the expected complex, Pt(**1**)$_2$ClMe (**7**).

***trans*-Pt(PEt$_3$)Cl$_2$(1) (10).** A solution of phosphole **1** (0.05 mL, 0.72 mmol) in 10 mL of dichloromethane was added dropwise at room temperature (22 °C) to a solution of $[Pt(PEt_3)Cl_2]_2$ (0.138 g, 0.18 mmol) in 15 mL of dichloromethane and stirred for 4 h. 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 to give **10** as an off-white powder, (0.089 g, 86.3%), mp 122 °C (dec). Anal. Calcd for $C_{10}H_{21}Cl_2F_2N_2P_3Pt$: C, 21.21; H, 3.74; Cl 12.52; N, 4.95. Found: C, 21.35; H, 3.72; Cl, 12.62; N, 4.91. MS (FAB, *m*/*z*): 566 (M, 7%). IR data (CH_2Cl_2 cast, cm^{-1}): ν(P−F) 842 (s), 790 (s). NMR data ($CDCl_3$) are as follows. $^{31}P\{^1H\}$: P(σ^2) δ 265.81 (d, $^2J_{PP}$ 155 Hz), P(σ^4) δ 124.32 (ddt, Pt sat., $^2J_{PP}$ 155 Hz, $^1J_{\sigma^4PF}$ 1115 Hz, $^2J_{\sigma^4PPEt_3}$ 18 Hz, $^1J_{\sigma^4PPt}$ 5445 Hz), PEt$_3$ δ 18.40 (d, Pt sat., $^2J_{PP}$ 18 Hz, $^1J_{PPt}$ 3190 Hz). ^1H: C−C*H*$_3$ δ 2.48 (s), P(σ^2)−N−C*H*$_3$ δ 3.97 (d, $^3J_{PH}$ 8.0 Hz). $^{13}C\{^1H\}$: C−*C*H$_3$ δ 15.49 (s), P(σ^2)−N−*C*H$_3$ δ 44.88 (d, $^2J_{\sigma^2PC}$ 15 Hz), P−*C*−P δ 148.35 (d, $^1J_{\sigma^2PC}$ 31 Hz), N−*C*−CH$_3$ δ 154.48 (d, $^2J_{\sigma^2PC}$ 3 Hz, $^2J_{\sigma^4PC}$ 18 Hz). ^{19}F: δ −43.02 (dd, $^3J_{\sigma^2PF}$ 15 Hz, $^1J_{\sigma^4PF}$ 1115 Hz).

(10) Parameter Adjustment in NMR by Iteration Calculation (PANIC), Brüker Instrument Co., Karlsrühe, Germany.
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Table 1. $^{31}P\{^1H\}$ and ^{19}F NMR Data for Pt and Pd Complexes of 4-(Disubstituted phosphino)-2,5-dimethyl-2*H*-1,2,3σ^2-diazaphospholes[a,b]

complex	no.	$\delta(\sigma^2P)$ (ppm)	$\delta(\sigma^4P)$ (ppm)	$^2J_{PP}$ (Hz)	δ(F) (ppm)	$^1J_{\sigma^4PF}$ (Hz)	$^3J_{\sigma^2PF}$ (Hz)
cis-Pt(**1**)$_2$Cl$_2$	**4**	271.21[c]	159.29[d]	150	−36.13[c]	1130	
cis-Pd(**1**)$_2$Cl$_2$	**5**	268.88[c]	144.33[d]	158	−39.42[c]	1184	nr
Pd(**1**)$_4$	**6**	258.90[c]	188.90[d]	116	−43.24[c]	1131	nr
Pt(**1**)$_4$	**9**	267.88[c]	164.90[d]	159	−43.02[c]	1130	nr
trans-Pt(**1**)(PEt$_3$)Cl$_2$	**10**	265.81[c]	124.32[d]	155	−43.02[i]	1115	15
trans-Pd(**1**)(PEt$_3$)Cl$_2$	**11**	266.05[c]	160.23[d]	150	−38.31[i]	1125	13
trans-Pt(**2**)$_2$Cl$_2$	**12**	249.69[e]	80.63[e]	57[c,j]			
trans-Pd(**2**)$_2$Cl$_2$	**13**	249.72[e]	86.94[e]	51[c,j]			
trans-Pt(**2**)$_2$ClMe	**14**	267.88[e]	75.21[e]	53[c,j]			
trans-Pd(**3**)$_2$Cl$_2$	**15**	256.43[e]	131.22[e]	51[c,j]			
cis-Pt(**3**)$_2$Cl$_2$	**16**	249.69[c]	80.63[c]	58			

[a] Chemical shifts δ in ppm in $CDCl_3$ with respect to 85% H_3PO_4. [b] In $CDCl_3$. [c] Doublet. [d] Doublet of triplets. [e] Second order. [f] Doublet of doublet of doublets. [g] Doublet of doublet of triplets. [h] Doublet of doublet of of doublet of doublets. [i] Doublet of doublets. [j] $|^2J_{\sigma^2P\sigma^4P} + {}^4J_{\sigma^2P\sigma^4P'}|$.

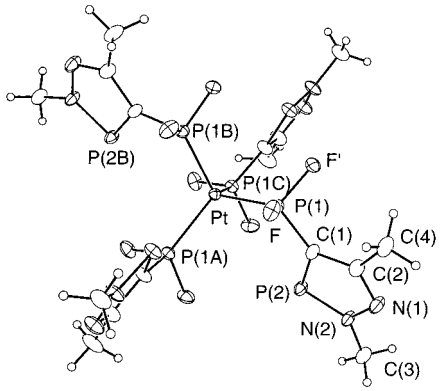


Figure 1. ORTEP[41] representation of the molecular structure of tetrakis(difluoro{2,5-dimethyl-2*H*-1,2,3σ^2-diazaphosphol-4-yl}phosphine)-platinum(0) (**9**). Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are shown with arbitrarily small thermal parameters.

***trans*-Pd(PEt$_3$)Cl$_2$(1) (11).** A solution of phosphole **1** (0.05 mL, 0.36 mmol) in 10 mL of dichloromethane was added dropwise at room temperature (22 °C) to a solution of [Pd(PEt$_3$)Cl$_2$]$_2$ (0.216 g, 0.36 mmol) in 15 mL of dichloromethane and stirred for 4 h. 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 to give **11** as a yellowish powder (0.269 g, 78.3%), mp 111 °C (dec). Anal. Calcd for $C_{10}H_{21}Cl_2F_2N_2P_3Pd$: C, 25.15; H, 4.43; Cl 14.85; N, 5.87. Found: C, 25.11; H, 4.56; Cl 14.99; N, 5.78. MS (FAB, *m*/*z*): 479 (M + 1, 9%). IR data (CH_2Cl_2 cast, cm^{-1}): ν(P−F) 849 (s), 788 (s). NMR data ($CDCl_3$) are as follows. $^{31}P\{^1H\}$: P(σ^2) δ 266.05 (d, $^2J_{PP}$ 153 Hz), P(σ^4) δ 160.23 (dt, broad, $^2J_{PP}$ 153 Hz, $^1J_{PF}$ ∼1125 Hz), PEt$_3$ δ 42.62 (s). ^1H: C−CH_3 δ 2.48 (s), P(σ^2)−N−CH_3 δ 3.97 (d, $^3J_{PH}$ 8.0 Hz). $^{13}C\{^1H\}$: C−CH_3 δ 15.61 (s), P(σ^2)−N−CH_3 δ 44.88 (d, $^2J_{\sigma^2PC}$ 18 Hz), P−*C*−P δ 148.35 (d, $^1J_{\sigma^2PC}$ 30 Hz), N−*C*−CH$_3$ δ 152.53 (d, $^2J_{\sigma^2PC}$ 4 Hz, $^2J_{\sigma^4PC}$ 12 Hz). ^{19}F: δ −38.31 (dd, $^3J_{\sigma^2PF}$ 15 Hz, $^1J_{\sigma^4PF}$ ∼1125 Hz).

***trans*-Pt(2)$_2$Cl$_2$, (12).** A solution of phosphole **2** (0.25 mL, 1.2 mmol) in 10 mL of dichloromethane was added dropwise at room temperature (22 °C) to a solution of Pt(cod)Cl$_2$ (0.225 g, 0.60 mmol) in 15 mL of dichloromethane and stirred for 4 h. 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 to give **12** as an off-white powder (0.344 g, 78.6%), mp 191−193 °C (dec). Calcd for $C_{16}H_{36}Cl_2N_8P_4Pt$: C, 26.31; H, 4.97; Cl 9.71; N, 15.34. Found: C, 26.51; H, 5.09; Cl 9.75; N, 15.37. MS (FAB, *m*/*z*): 730 (M + 1, 11%). NMR data ($CDCl_3$) are as follows. $^{31}P\{^1H\}$: P(σ^2) δ 249.69 (t, $|^2J_{\sigma^2P\sigma^4P} + {}^4J_{\sigma^2P\sigma^4P'}|$ 57 Hz), P(σ^4) δ 80.63 (dt, Pt sat. $|^2J_{\sigma^2P\sigma^4P} + {}^4J_{\sigma^2P\sigma^4P'}|$ 57 Hz, $^1J_{\sigma^4PPt}$ 2918 Hz). ^1H: C−CH_3 δ 2.43 (dd, $4J_{PH}$ 0.9 Hz), P(σ^2)−N−CH_3 δ 4.02 (d, $^3J_{PH}$ 12.2 Hz), P(σ^4)−N−CH_3 δ 2.76 (d, $^3J_{\sigma^4PH}$ 7.2 Hz). $^{13}C\{^1H\}$: C−CH_3 δ 14.73 (s), P(σ^2)−N−CH_3 δ 41.92 (d, $^2J_{PC}$ 18 Hz), P−*C*−P δ 148.45 (dd, $^2J_{\sigma^2PC}$ 4 Hz, $^2J_{\sigma^4PC}$ 14 Hz), N−*C*−CH$_3$ δ 156.27 (s). ^{195}Pt: δ 179.04 (t, $^1J_{\sigma^4PPt}$ 2918 Hz).

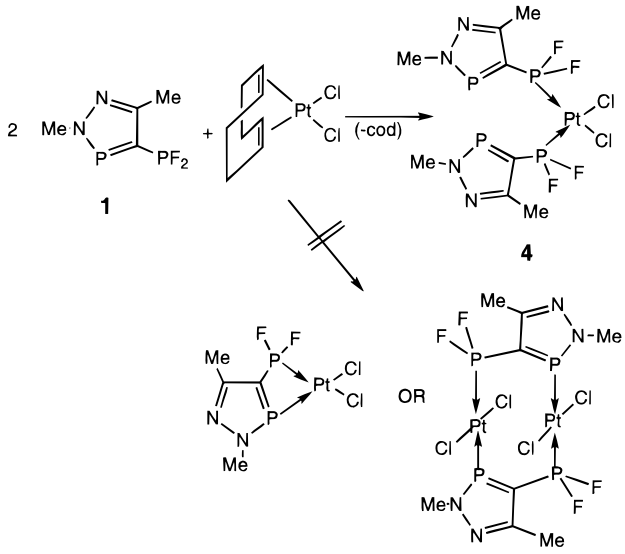
***trans*-Pd(2)$_2$Cl$_2$ (13).** A solution of phosphole **2** (0.25 mL, 1.2 mmol) in 10 mL of dichloromethane was added dropwise at room temperature (22 °C) to a solution of Pd(cod)Cl$_2$ (0.171 g, 0.60 mmol) in 15 mL of dichloromethane and stirred for 4 h. The solution was concentrated to ∼5 mL, and hexane was added until the solution became slightly turbid. The solution was stored at −40 °C overnight to give **13** as light yellow crystals (0.260 g, 67.6%), mp 186 °C (dec). Anal. Calcd for $C_{16}H_{36}Cl_2N_8P_4Pd$: C, 29.95; H, 5.65; Cl 11.05; N, 17.46. Found: C, 29.92; H, 5.72; Cl 11.35; N, 17.49. MS (FAB, *m*/*z*): 641 (M + 1, 5%). NMR data ($CDCl_3$) are as follows. $^{31}P\{^1H\}$: P(σ^2) δ 249.72 (t, $|^2J_{\sigma^2P\sigma^4P} + 4J_{\sigma^2P\sigma^4P'}|$ 51 Hz), P(σ^4) δ 86.91 (t, $|^2J_{\sigma^2P\sigma^4P} + 4J_{\sigma^2P\sigma^4P'}|$ 51 Hz). ^1H: C−CH_3 δ 2.43 (dd, $^4J_{PH}$ 0.9 Hz), P(σ^2)−N−CH_3 δ 4.03 (d, $^3J_{\sigma^2PH}$ 12.2 Hz), P(σ^4)−N−CH_3 δ 2.68 (d, $^3J_{\sigma^4}$ 7.8 Hz). $^{13}C\{^1H\}$: C−CH_3 δ 14.37 (s), P(σ^2)−N−CH_3 δ 41.88 (d, $^2J_{\sigma^2PC}$ 18 Hz), P−*C*−P δ 143.45 (dd, $^2J_{\sigma^2PC}$ 5 Hz, $^2J_{\sigma^4PC}$ 14 Hz), N−*C*−CH$_3$ δ 156.72 (s).

***trans*-PtMeCl(2)$_2$ (14).** A solution of phosphole **2** (0.25 mL, 1.2 mmol) in 10 mL of dichloromethane was added dropwise at room temperature (22 °C) to a solution of Pt(cod)ClMe (0.117 g, 0.30 mmol) in 15 mL of dichloromethane and stirred for 4 h. 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 to give **14** as a light yellow powder (0.194 g, 77.6%), mp 156 °C (dec). Anal. Calcd for $C_{17}H_{39}ClN_8P_4Pt$: C, 28.76; H, 5.54; Cl 4.99; N, 15.78. Found: C, 28.60; H, 5.59; Cl 4.35; N, 15.86. MS (FAB, *m*/*z*): 711 (M + 1, 5%). NMR data ($CDCl_3$) are as follows. $^{31}P\{^1H\}$: P(σ^2) δ 248.29 (t, $|^2J_{\sigma^2P\sigma^4P} + {}^4J_{\sigma^2P\sigma^4P'}|$ 53 Hz), P(σ^4) δ 75.21 (t Pt sat., $|^2J_{\sigma^2P\sigma^4P} + {}^4J_{\sigma^2P\sigma^4P'}|$ 53 Hz, $^1J_{\sigma^4PPt}$ 3351 Hz). ^1H: C−CH_3 δ 2.34 (dd, $^4J_{PH}$ 0.9 Hz), P(σ^2)−N−CH_3 δ 4.03 (d, $^3J_{\sigma^4PH}$ 12.2 Hz), P(σ^4−N−CH_3 δ 2.74 (d, $^3J_{\sigma^4PH}$ 7.6 Hz). $^{13}C\{^1H\}$: C−CH_3 δ 14.37 (s), P(σ^2)−N−CH_3 δ 41.78 (d, $^2J_{\sigma^2PC}$ 17 Hz), P−*C*−P δ 144.53 (dd, $^2J_{\sigma^2PC}$ 4 Hz, $^2J_{\sigma^4PC}$ 13 Hz), N−*C*−CH$_3$ δ 156.72 (s). ^{195}Pt: δ 354.40 (ttq, $^1J_{\sigma^4PPt}$ 3351 Hz, $^3J_{\sigma^2PPt}$ 50 Hz, $^2J_{PtH}$ 82 Hz).

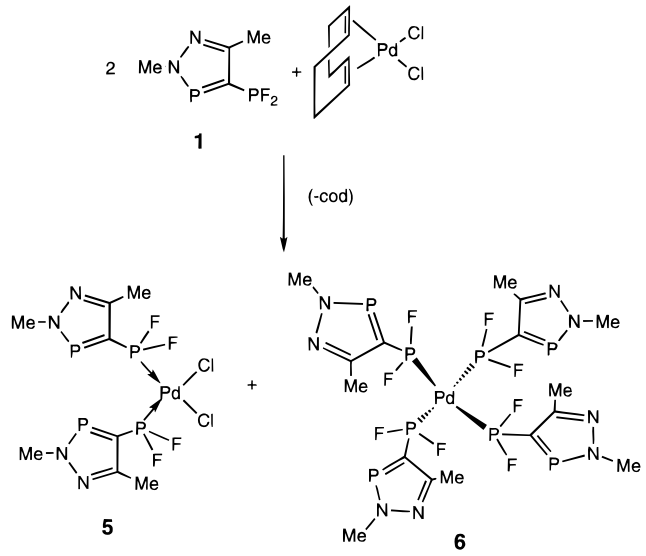
***trans*-PdCl$_2$(3)$_2$ (15).** A solution of phosphole **3** (0.193 g, 0.57 mmol) in 10 mL of dichloromethane was added dropwise at room temperature (22 °C) to a solution of Pd(cod)Cl$_2$ (0.081 g, 0.28 mmol) in 15 mL of dichloromethane and stirred for 4 h. The solution was reduced to ∼3 mL, and 10 mL of hexanes was added. The solution was stored overnight at room temperature during which time **15** formed as a yellow powder (1.889 g, 78.3%), mp 168 °C (dec). Anal. Calcd for $C_{16}H_{20}Cl_2F_{12}N_4O_4P_4Pd$: C, 22.31; H, 2.34; Cl, 8.23, N, 6.50. Found: C, 22.12; H, 2.30; Cl, 8.42, N, 6.62. MS (FAB, *m*/*z*): 861 (M, 5%). NMR data ($CDCl_3$) are as follows. $^{31}P\{^1H\}$: P(σ^2) δ 256.43 ("t", $|^2J_{\sigma^2\sigma^4P} + {}^4J_{\sigma^2P\sigma^4P'}|$ 51 Hz), P(σ^4) δ 131.22 ("t", $|^2J_{\sigma^2\sigma^4P} + {}^4J_{\sigma^2P\sigma^4P'}|$ 51 Hz). ^1H: C−CH_3 δ 2.60 (s), P(σ^2)−N−CH_3 δ 4.06 (d, $^3J_{\sigma^2PH}$ 5.2 Hz) P(σ^4)−N−O−CH_2 δ 4.6−4.3 (m (broad)). $^{13}C\{^1H\}$: C−CH_3 δ 15.49 (s), P(σ^2)−N−CH_3 δ 44.36 (d, $^2J_{\sigma^2PC}$ 18 Hz), P−*C*−P δ 148.62 (dd, $^1J_{\sigma^2PC}$ 57 Hz, $^1J_{\sigma^4PC}$ 35 Hz), N−*C*−CH$_3$ δ 156.48 (dd, $^2J_{\sigma^2PC}$ 5 Hz, $^2J_{\sigma^4PC}$ 17 Hz), O−*C*H$_2$−CF$_3$, δ 63.32 (dq, $^2J_{PC}$ 8 Hz, $^2J_{CF}$ 36 Hz), O−CH$_2$−*C*F$_3$ δ 123.52, (dq, $^3J_{PC}$ 6 Hz, $^1J_{CF}$ 278 Hz), $^2J_{\sigma^2PC}$ 5 Hz). ^{19}F: δ −74.50 (s).

***cis*-PtCl$_2$(3)$_2$ (16).** A solution of phosphole **3** (0.151 g, 0.44 mmol) in 10 mL of dichloromethane was added dropwise at room temperature (22 °C) to a solution of Pt(cod)Cl$_2$ (0.083 g, 0.22 mmol) in 15 mL of dichloromethane and stirred for 4 h. The solution was concentrated to ∼5 mL, and hexane was added until the solution became slightly turbid.

Scheme 1. Reaction of **1** with $Pt(cod)Cl_2$



Scheme 2. Reaction of **1** with $Pd(cod)Cl_2$



The solution was stored at −40 °C overnight to give **16** as an off-white powder (0.162 g, 77.6%), mp 172 °C (dec). Anal. Calcd for $C_{16}H_{20}Cl_2F_{12}N_4O_4P_4Pt$: C, 20.22; H, 2.12; Cl 7.46, N, 5.90. Found: C, 20.35; H, 2.25; Cl 7.35; N, 6.01. MS (FAB, *m/z*): 951 (M + 1, 13%). NMR data ($CDCl_3$) are as follows. $^{31}P\{^1H\}$: P(σ^2) δ 256.78 (d, $^2J_{PP}$ 58 Hz,), P(σ^4) δ 104.37 (d, Pt sat., $^2J_{PP}$ 58 Hz, $^1J_{PPt}$ 4811 Hz). ^1H: C−CH_3 δ 2.65 (dd, $^4J_{PH}$ 0.9 Hz), P(σ^2)−N−CH_3 δ 4.09 (d, $^3J_{\sigma^2PH}$ 8.4 Hz), P(σ^4−N−O−CH_2 δ 4.6−4.4 (m (broad)). $^{13}C\{^1H\}$: C−*C*H_3 δ 14.53 (s), P(σ^2)−N−*C*H_3 δ 41.36 (d, $^2J_{\sigma^2PC}$ 18 Hz), P−*C*−P δ 144.65 (dd, $^2J_{\sigma^2PC}$ 59 Hz, $^2J_{\sigma^4PC}$ 45 Hz), N−*C*−CH_3 δ 156.72 (dd, $^2J_{\sigma^2PC}$ 5 Hz, $^2J_{\sigma^4PC}$ 18 Hz), O−*C*H_2−CF_3, δ 63.33, (dq, $^2J_{PC}$ 8 Hz, $^2J_{CF}$ 36 Hz), O−CH_2−*C*F_3 δ 123.46 (dq, $^3J_{CP}$ 6 Hz, $^1J_{CF}$ 279 Hz), $^2J_{\sigma^2PC}$ 5 Hz). ^{19}F: δ −74.52 (s).

Results and Discussion

Complexation and Reduction Chemistry of 4-(Difluorophosphino)-2,5-dimethyl-2*H*-1,2,3σ^2-diazaphosphole (1). When **1** was combined with $Pt(cod)Cl_2$, smooth displacement of the cyclooctadienyl ligand occurred to yield the disubstituted cis-complex Pt(**1**)$_2$Cl$_2$ (**4**) (Scheme 1). Although **1** offers an appropriate bite angle between two donor centers that could lead to bimetallic bridged structures similar for example to the dimers formed by dppm with Pt^{II},[22] the NMR spectra of the reaction product did not reveal any species of this type.

In previous work[4,5] with related simple diazaphosphole ligands, monomeric and dimeric Pt^{II} complexes were formed without replacement of the original phosphine ligands. Only the dimer bridges were cleaved by the phospholes indicating that the dicoordinate phosphorus center is a very weak base.[5] Also, in those cases, Pt^{II} was not reduced.[5] Pt^0 precursors gave, with the diazaphosphole, a series of Pt^0L_4 complexes in which the initially coordinated phosphines were replaced by only one or two phospholes; complete replacement of the phosphines present on the metal precutsor complex was not achieved suggesting again that the phospholes are not strongly basic ligands.[4]

The $^{31}P\{^1H\}$ NMR spectrum of **4** was characteristic of a *cis*-diphosphine complex of Pt^{II}. Coordination through the exocyclic phosphine was indicated by the fact that there was only a small downfield shift of the σ^2P resonance (271.21 ppm) and no Pt satellites were associated with this signal. The exocyclic phosphorus center (159.3 ppm) in the complex displays a large upfield shift of the resonance relative to the free ligand, and in addition, a very large phosphorus−platinum one-bond coupling constant ($^1J_{PPt}$ = 5064 Hz) is observed indicating that the exocyclic phosphine is bound to Pt. In the complex, $^2J_{PP}$ was larger (150 Hz) and $^1J_{PF}$ was smaller (1125 Hz) than the values displayed by the free ligand. The $^1J_{PPt}$ value in this complex is much larger than the typical range of 2300−3600 Hz generally observed for *cis*-$PtCl_2(PR_3)_2$ complexes,[23] and indeed there are not many platinum complexes which have $^1J_{PPt}$ values greater than 5000 Hz.[24−26] Notably, the Pt phosphole complexes also display large $^1J_{PPt}$ coupling constants.[4,5]

The ^{19}F NMR chemical shift signal for the fluorine atoms was centered at −35.86 ppm and showed coupling to both phosphorus centers ($^3J_{\sigma^2PF}$ = 12 Hz, $^1J_{PF}$ = 1125 Hz). These values are typical for such complexes and are not much altered from the free ligand.

The reaction of **1** with $Pd(cod)Cl_2$ was much more complex. The initial yellow solution of the palladium precursor changed first to pale yellow and then, over a period of 1 h, a deep maroon solution formed. The $^{31}P\{^1H\}$ NMR spectrum of this maroon solution showed that there was a mixture of two species, one being the expected palladium(II) complex, *cis*-Pd(**1**)$_2$Cl$_2$ (**5**). The other was the reduced palladium(0) complex, Pd(**1**)$_4$ (**6**) (Scheme 2).

The $^{31}P\{^1H\}$ NMR spectrum of this *cis*-Pd(**1**)$_2$Cl$_2$ complex (**5**) was a typical AMX_2 spin pattern. The $^{31}P\{^1H\}$ NMR resonance for the exo-phosphorus center in **5** appeared as a doublet of triplets and showed an upfield shift (to 144.33 ppm) while the signal for the σ^2P center (a doublet) was shifted downfield to 267.88 ppm and was broadened. The value of $^2J_{PP}$ (158 Hz) increased relative to the starting phosphine **1**. The one-bond phosphorus fluorine coupling constant had also increased slightly (1184 Hz) in the complex relative to the free ligand. The ^{19}F NMR chemical shift signal was centered at −36.42 ppm, and again both phosphorus centers were coupled to the fluorine ($^3J_{\sigma^2PF}$ = 15 Hz, $^1J_{PF}$ = 1182 Hz).

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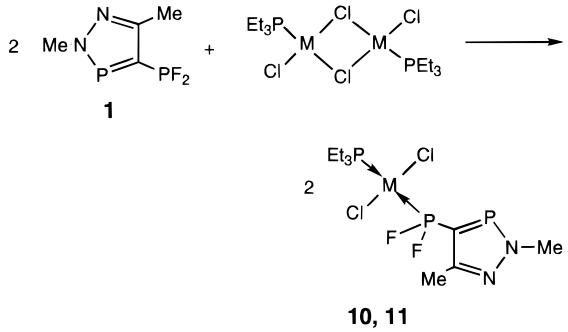
Scheme 3. Reactions of the Ethylphosphine Chloro Dimers of Pd and Pt with **1** (M = Pt (**10**), M = Pd(**11**))



Phosphorus NMR signals arising from both the endo- and the exo-phosphorus centers in the Pd(0) complex (**6**) appeared much broader than those for the analogous Pd^{II} complex **5**, but no free phosphole signal was observed in contrast to behavior of previously investigated Pd^0L_4 complexes of aryl- and alkylphosphines.[27] These broad signals were not sharpened by cooling the $^{31}P\{^1H\}$ NMR sample to −75 °C in either of the Pd^0 or the Pd^{II} cases so it does not appear that there is a facile ligand exchange. Attempts to crystallize either of these palladium complexes resulted only in a maroon oil; thus, complexes **5** and **6** were not separated from this mixture.

An authentic sample of the pure Pd^0 complex $Pd(\mathbf{1})_4$ (**6**) was easily obtained however as a wine-red powder from the reaction of $Pd_2(dba)_3{\cdot}CHCl_3$ with 4 equiv of **1**. The $^{31}P\{^1H\}$ NMR of a solution of pure **6** showed the same broadened signal previously observed in the mixed product. The doublet of triplets for the exo-phosphorus center (202.45 ppm) and the broadened doublet for the σ^2P center (261.17 ppm) confirm the assignments derived from the mixture. Changes in chemical shifts and coupling constants similar to those dispayed by the Pt system were observed.

It also is notable that the reaction of $Pt(cod)Cl_2$ with **1** showed no evidence for reduction of the metal whereas reaction of $Pd(cod)Cl_2$ with **1** gave a reduced product. We show below that reduction of Pt^{II} to Pt^0 complex occurs under different conditions.

The phospholylphosphine **1** reacted with the bridged dimers $[M(PEt_3)Cl_2]_2$ (M = Pt or Pd) (Scheme 3) to yield the *trans*-phosphine complexes of the metals with two different coordinated phosphines. In these reactions, the only process is cleavage of the Cl bridge; the original phosphines are not displaced. These reactions are parallel to those described with the simple phosphole[5] except that in this previous study the dicoordinate phosphole center acted as the coordination site, there being no exo-cyclic phosphorus in that case. Thus *trans*-$M(PEt_3)(\mathbf{1})Cl_2$ (**10**, M = Pt; **11**, M = Pd), each of which contain a coordinated exo-cyclic phosphorus of the diazaphospholylphosphine **1** trans-disposed to Et_3P, were obtained in good yield. The $^{31}P\{^1H\}$ NMR spectrum of the platinum complex again showed that coordination to the Pt had occurred through the exo-cyclic phosphine center and that two phosphine centers were attached to the metal. In the platinum complex **10**, the exo-cyclic phosphorus center signal of ligand **1** was shifted upfield approximately 85 ppm (to 124.32 ppm) whereas the σ^2 phosphorus resonance shifted upfield by only 10 ppm (to 265.81 ppm) relative to the free ligand. In contrast, the resonance signal for the PEt_3 ligand was shifted by 10 ppm downfield (to 18.4 ppm) relative to that found in the starting platinum complex. There was a large increase in the two-bond $\sigma^2P-\sigma^4P$ coupling constant (155 Hz) and a decrease of $^1J_{PF}$ to 1115 Hz. Again the $^1J_{PPt}$ coupling between Pt and the coordinated P^{III} of **1** was large (5445 Hz) which also confirmed that the exo-cyclic phosphorus center of **1** was the coordinate link. Coupling between Pt and the phosphorus of PEt_3 was also easily identified, but the value had decreased to 3190 Hz, smaller than the value of 3845 Hz in the parent complex. Also observed was a moderate (18 Hz) $^2J_{P(PEt_3)}$ coupling between the two coordinated phosphine centers in the complex. The opposite trend of the Pt−P coupling constants displayed by the two ligands in the trans complex is consistent with the fact that both trans ligands of square planar complexes are competing for the same metal d_π orbitals; if one is a stronger acceptor, it steals away interaction from its trans counterpart and the weaker platinum−phosphorus interaction is reflected in a decreased coupling constant. In contrast cis ligands do not compete for the same electron density and both ligands can maximize their Pt−P coupling constants. When metal−halogen bonds are involved, the small π component in these bonds also offers minimal competition for back-bonding with platinum; thus, the platinum−phosphorus interactions can be enhanced.

The ^{19}F NMR signals of the platinum complex **10** were centered at −38.21 ppm and showed coupling to both phosphorus centers of the diazaphospholylphosphine ($^3J_{\sigma^2PF}$ = 15 Hz, $^1J_{PF}$ = 1115 Hz). The values are typical for Pt−fluorophosphine complexes.

The pattern of the $^{31}P\{^1H\}$ NMR spectrum and the phosphorus shift values of the palladium complex **11** were very similar to those of the analogous Pt complex, **10**. The NMR signals were also slightly broader than usual. The magnitudes of the upfield NMR shifts for the exo-cyclic phosphorus signal of 49 ppm (to 160.23 ppm) and for the σ^2P of 10 ppm (to 266.05 ppm) were parallel to those displayed by the Pt analogue. The phosphorus chemical shift for the PEt_3 ligand (at 42.62 ppm) remained relatively unchanged relative to the value observed for the starting material. The $^2J_{\sigma^2PP}$ value also increased (150 Hz) relative to the free ligand as was observed with the platinum complex. In contrast to the $^{31}P\{^1H\}$ NMR spectrum of $Pt(PEt_3)(\mathbf{1})Cl_2$ (**10**), phosphorus−phosphorus coupling between **1** and PEt_3 ($^2J_{PPEt_3}$) was not observed possibly due to the breadth of the resonance which would prevent the resolution of a small coupling. The ^{19}F NMR of **11** gave a fluorine signal at −35.78 ppm which was a doublet of doublets due to coupling with both phosphorus centers of the diazaphospholylphosphine ($^1J_{PF}$ = 1125 Hz, $^3J_{PF}$ = 13 Hz). There was little change in the $^1J_{PF}$ value in the complex relative to that of the free phosphine.

The reaction of Pt(cod)ClMe with **1** gave, ultimately, an unexpected reductive−elimination reaction product, $Pt^0(\mathbf{1})_4$ (**9**), isolated from the reaction mixture as an orange crystalline solid. Complex **9** also showed slightly broad ^{31}P NMR spectra, but no evidence for free phosphole was observed in contrast to the typical behavior of Pt(0) complexes of organophosphines.[27] The ^{31}P NMR spectrum of **9** was characterized by a large value of $^1J_{PPt}$ (5050 Hz) and by an increased $^2J_{PP}$ (159 Hz) coupling. The signal for the σ^2 phosphole center was shifted slightly upfield, and the direct $^1J_{PF}$ coupling was reduced (1130 Hz) relative to the free ligand.

When less than 2 equiv of **1** was used relative to Pt(cod)ClMe, an intermediate complex $Pt(\mathbf{1})_2ClMe$ (**7**) was observed, identified in solution by NMR parameters. This complex could not be isolated; attempts to isolate the intermediate resulted only in the crystallization of **9**, so structural characterization of this interesting species could not be achieved. The $^{31}P\{^1H\}$ NMR

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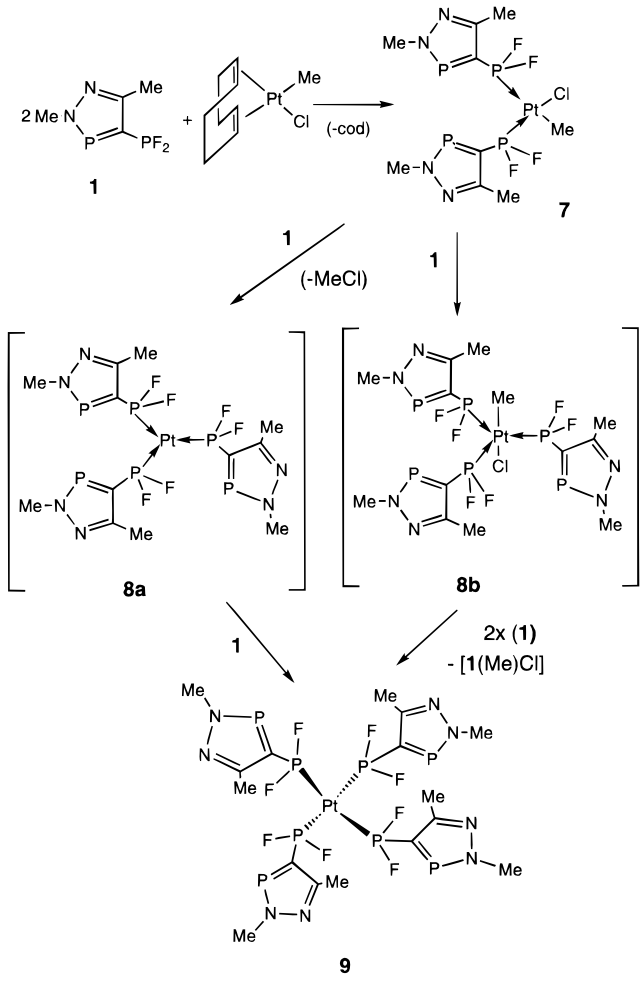
Scheme 4. Pathways for the Reaction of **1** with Pt(cod)ClMe to Pt(**1**)$_4$ through Putative $Pt^{II}L_3$ or Pt^0L_3 Intermediates[a]



[a] MeCl may be liberated by direct reductive elimination or through the formation of the phosphorane represented [**1**(Me)Cl].

spectrum of **7** identified one complexed σ^4 phosphorus center at 135.6 ppm ($^1J_{PPt}$ 6089 Hz), while the other σ^4 resonance was observed at 186.61 ppm ($^1J_{PPt}$ 2511 Hz). The difference in these two resonance signals for the exo-phosphorus centers can be attributed to the greater trans-influence[28] of the methyl group (a ligand with minimal π-acceptor properties) relative to the chloride.[28] This strong covalent bond induces a large metal π component in the trans bond which will be weakened.[29] The chemical shift for the resonance for the σ^2P center in this complex **7** remained the same throughout with only a slight broadening of the peak (265 ppm) illustrating that this center is insulated from the electronic effects at the metal.

Possible pathways for the formation of **9** are outlined in Scheme 4. The reaction begins with the simple substitution of the cod ligand with two phospholylphosphines to form **7**. Several different subsequent pathways can be proposed, for example, reductive elimination of MeCl to yield the tricoordinate complex **8a** which then binds an additional phosphine to crystallize the finally isolated complex **9**. Alternatively, since we were unable to observe MeCl (and in view of the fact that a similar reduction also occurs in the case of the reaction to form Pd(**1**)$_2$Cl$_2$ which could imply the improbable reductive elimination of Cl_2), we can suggest that the reaction proceeds through an initial base coordination of another 1 mol of phosphine to form a five coordinate Pt^{II} complex (**8b**), which may then undergo a reductive elimination of chloromethane to produce a tricoordinate intermediate. This species then readily adds a fourth phosphine. More likely, however, is a redox process on the five coordinate Pt center which transfers the elements of MeCl to phosphorus thereby forming a phosphorane of the type (phosphole)PF_2(Me)Cl which is eliminated. The resultant tricoordinate Pt intermediate is stabilized and crystallized with another 1 mol of phosphine as previously suggested. The analogous process in the Pd case would be the reasonable formation of a phosphorane of the type (phosphole)PF_2Cl_2 by the abstraction of the two chlorides from the analogous five coordinate Pd intermediate. Precedent for the formation of the halogeno−phosphorane exists in neat reaction systems,[30] but we were not able to identify any phosphorane species. It is possible that these species were decomposed by subsequent reactions or by the solvent used. Further work on these interesting systems would clearly be warranted.

The reductive elimination process leading to **9** in our system resembles the elimination of biphenyl from (phenyl)$_2Pt^{II}$(fluorophosphine)$_2$ complexes reported previously.[9] Presumably, the more common reduction reaction of platinum phosphine complexes involves reduction of platinum from the +4 to the +2 oxidation state rather than from Pt^{II} to Pt^0.[31] Direct reduction of Pt^{II} to Pt^0 complexes with fluorinated phosphines is however known and has been exploited previously.[7,8,32] Also, it has long been known that known that phosphorus trifluoride or CF_3PF_2 (neat) react with platinum(II) chloride complexes at elevated temperatures with reduction of platinum to give Pt^0(phosphine)$_4$ complexes.[8,30] The other product was the chlorofluorophosphorane.[30] These results and also our results from other systems[1−3] suggest clearly that the ligating character of **1** is very similar to that of PF_3 and phosphites. It is therefore not ultimately surprising that Pt^{II} can be reduced to Pt,[0] but the facility of the reduction reaction displayed by **1** is notable. The fact that the ligand appears to be free of large steric constraints and that products are potentially solid crystalline products suggests that **1** may be a very useful fluorophosphine ligand.

Complex **9** was structurally characterized, and it transpires that this complex represents one of the very few homoleptic Pt^0L_4 complexes to be structurally characterized in the solid state and the first to be fully reported.[33] In total however, not many complexes of the Pt^0 system have been structurally characterized.[9,34−36] Most contain, in general, bidentate chelating ligands or a mix of monodentate and bidentate phosphines,[35,36] and so the structures obtained may suffer from geometrical constraints imposed by the chelating ligand or, alternatively,

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Table 2. Crystallographic Experimental Details for **9**

A. Crystal Data	
formula	$C_{16}H_{28}F_8N_8O_2P_8Pt$
fw	959.31
cryst dimens (mm)	0.33 × 0.26 × 0.26
cryst system	tetragonal
space group	$I\bar{4}2m$ (No. 121)
unit cell params[a]	
a (Å)	11.961(2)
c (Å)	15.034(3)
V (Å^3)	2150.8(6)
Z	2
ρ_{calcd} (g cm^{-3})	1.481
μ (mm^{-1})	3.619
B. Data Collection and Refinement Conditions	
diffractometer	Enraf-Nonius CAD4[b]
radiation (λ (Å))	Mo Kα (0.710 73)
monochromator	incident-beam, graphite crystal
temp (°C)	−50
scan type	$\theta-2\theta$
data collcn 2θ limit (deg)	50.0
tot. data collcd	4256 ($-14 \le h \le 14$, $-14 \le k \le 14$, $-17 \le l \le 17$)
independent reflctns	1021
no. of observns (NO)	1009 ($F_o^2 \ge 2\sigma(F_o^2)$)
structure solution method	direct methods (SHELXS-86[c])
refinement method	full-matrix least-squares on F^2 (SHELXL-93[d])
abs corr method	DIFABS[e]
range of abs corr factors	1.157−0.815
data/restraints/params	1021 [$F_o^2 \ge -3\sigma(F_o^2)$]/0/61
goodness-of-fit (S)[f]	1.299 [$F_o^2 \ge -3\sigma(F_o^2)$]
final R indices[g]	
$F_o^2 > 2\sigma(F_o^2)$	$R_1 = 0.0381$, w$R_2 = 0.1180$
all data	$R_1 = 0.0395$, w$R_2 = 0.1188$
largest diff peak and hole (e Å^{-3})	1.570 and −1.160

[a] Obtained from least squares refinement of 24 reflections with $18.0° < 2\theta < 26.7°$. [b] Programs for diffractometer operation and data collection were those supplied by Enraf-Nonius. [c] Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467. [d] Sheldrick, G. M. SHELXL-93. Program for crystal structure determination. University of Göttingen, Germany, 1993. Refinement on F_o^2 for all reflections (all of these having $F_o^2 < -3\sigma(F_o^2)$). Weighted R-factors wR_2 and all goodnesses of fit S are based on F_o^2; conventional R-factors R_1 are based on F_o, with F_o set to zero for negative F_o^2. The observed criterion of $F_o^2 > 2\sigma(F_o^2)$ is used only for calculating R_1 and is not relevant to the choice of reflections for refinement. R-factors based on F_o^2 are statistically about twice as large as those based on F_o, and R-factors based on all data will be even larger. [e] Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158−166. [f] $S = [\sum w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0769P)^2]^{-1}$, where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$). [g] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; w$R^2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^4)]^{1/2}$.

suffer reduced symmetry because of the difference in the ligating character within the collection of monodentate ligands.[4] Related complexes such as $Pt(CF_3PF_2)_4$[30] were not structurally characterized because of their volatility. The structure of $Pt(PF_3)_4$, also a very volatile species, was twice determined by electron diffraction some years ago.[37,38]

Complex **9** crystallized in the space group, $I\bar{4}2m$ (see Tables 2 and 3). The solid-state structure revealed the expected tetrahedral Pt^0 center, illustrated in Figure 1. The angles about the platinum, P(1A)−Pt−P(1) and P(1B)−Pt−P(1), are 111.71(8) and 105.1(2), respectively, indicating a slightly squashed tetrahedron about the Pt. The phosphole ligands are displaced about the center in a very symmetrical environment, and small

Table 3. Selected Interatomic Distances and Angles for Tetrakis(difluoro{2,5-dimethyl-2*H*-1,2,3σ^2-diazaphosphol-4-yl}-phosphine)platinum(0) (**9**)

Distances (Å)			
Pt−P(1)	2.237(3)	N(1)−N(2)	1.380(15)
P(1)−F	1.565(6)	N(1)−C(2)	1.33(2)
P(1)−C(1)	1.70(2)	N(2)−C(3)	1.42(2)
P(2)−N(2)	1.689(15)	C(1)−C(2)	1.45(2)
P(2)−C(1)	1.72(2)	C(2)−C(4)	1.50(2)
Angles (deg)			
P(1)^A−Pt−P(1)	117.1(8)	P(2)−N(2)−C(3)	127.9(12)
P(1)^B−Pt−P(1)	105.1(2)	N(1)−N(2)−C(3)	116.2(15)
Pt−P(1)−F	116.8(2)	P(1)−C(1)−P(2)	122.9(10)
Pt−P(1)−C(1)	121.2(6)	P(1)−C(1)−C(2)	131.5(14)
F−P(1−)F′	94.4(5)	P(2)−C(1)−C(2)	105.6(13)
F−P(1)−C(1)	101.7(4)	N(1)−C(2)−C(1)	119.1(15)
N(2)−P(2)−C(1)	91.7(8)	N(1)−C(2)−C(4)	113.7(14)
N(2)−N(1)−C(2)	107.6(15)	C(1)−C(2)−C(4)	127.1(5)
P(2)−N(2)−C(2)	115.9(11)		

interactions two pairs of F atoms may be responsible for the "squashing". As it sits in the unit cell the complex displays perfect S_4 symmetry. There are no unusual intermolecular contacts between molecules in the unit cell. The phosphole rings are planar, and the nitrogen in the 2-position is also planar (the sum of the angles about this nitrogen is 360°). The P(2)−N(2)-N(1) angle (115.9(11)°) is slightly wider than that of the phosphole itself (113.8°). The N(2)−P(2)−C(1) angle, 91.7-(8)°, is larger than that observed for the phosphole (90.4°).[13] The P(2)−N(2) bond distance of 1.689(15) Å suggests some multiple bond character when compared to the normally accepted P−N single bond value (1.77 Å); however, it is not as short as a typical P−N double bond (1.64 Å). The F−P−F′ bond angle is 94.4(5)°, while the P−F bond distance at 1.565-(6) Å is slightly longer than that which we observed for 4-(difluoro{*p*-cyanotetrafluorophenyl}iminophosphorano)-2,5-dimethyl-2*H*-1,2,3σ^2-diazaphosphole[2] but is similar to that found for the complex cyclopentadienylbis(κ^1P-4-(difluorophosphino)-2,5-dimethyl-2*H*-1,2,3σ^2-diazaphosphole rhodium(I), (CpRh-(**1**)$_2$).[3]

Complexation Reactions of 4-(Bis(dimethylamino)phosphino)-2,5-dimethyl-2*H*-1,2,3σ^2-diazaphosphole (2). The reaction of **2** with M(cod)Cl$_2$ (M = Pd, Pt) resulted in the simple displacement of the cyclooctadienyl ligand to give M(**2**)$_2$Cl$_2$ (M = Pt (**12**), Pd (**13**)). In each case, the $^{31}P\{^1H\}$ NMR spectrum showed a pattern of a deceptively simple second order "triplet" pattern which is characteristic of the trans-substituted square planar diphosphine complexes. Phosphorus chemical shifts were very similar; the exocyclic phosphine (which is the likely binding point) was found at 80.59 ppm for **12** and 86.94 ppm for **13**. The chemical shift for the endocyclic phosphorus centers were found at 248.88 ppm for **12** and at 249.63 ppm for **13**. The major line separations in each section ($|^2J_{\sigma^2P\sigma^4P} + 4J_{\sigma^2P\sigma^4P'}|$) were 57 Hz (**12**) and 51 Hz (**13**), respectively. The one-bond phosphorus−platinum coupling constant in **12** ($^1J_{PPt} = 2918$ Hz) clearly indicated the binding point in this complex, but the value is notably much smaller than that observed in the platinum complexes with **1** as discussed above. The ^{195}Pt NMR spectrum of **12** gave a chemical shift of 179.04 ppm.

The reaction of **2** with Pt(cod)ClMe produced only the complex Pt(**2**)$_2$ClMe (**14**) with no suggestion of reduction to Pt^0 as was observed with **1**. The $^{31}P\{^1H\}$ NMR signal for the coordinated exo-phosphorus center at 75.21 ppm appeared as a single deceptively simple triplet ($^2J_{\sigma^2P\sigma^4P} + 4J_{\sigma^2P\sigma^4P} = 53$ Hz) suggesting that the exo-phosphorus centers are equivalent and that the product complex is therefore the trans isomer. Were the cis isomer formed, as was the case in the reaction with **1**,

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the two coordinated phosphorus centers should have shown different shifts (as for **7** for example) and also the two $^1J_{PPt}$ values would be different as a result of the trans-influence. The ^{195}Pt NMR spectrum of **14** showed an $A_2D_2MX_3$ spin system in which the platinum is coupled to both phosphorus atoms ($^1J_{PPt}$ = 3554 Hz, $^3J_{PPt}$ = 50 Hz) as well as to the protons of the methyl group which is directly bound to Pt ($^2J_{HPt}$ = 83 Hz), thus giving rise to a splitting pattern of a triplet of triplets of quartets which is consistent with the trans structure.

Complexation Reactions of 4-((2,2,2-Trifluoroethoxy)-phosphino)-2,5-dimethyl-2*H*-1,2,3σ^2-diazaphosphole (3). The fluorinated alkoxy-substituted diazaphospholylphosphine **3** has a more basic exocyclic phosphine center than that in **1**, but it is less basic than the amino derivative **2**. This substituent is often used in phosphorus chemistry to stabilize a high coordination environment[39] so we might expect the ligand to behave in a fashion similar to **1**. Furthermore, this alkoxyphosphine center is not as bulky as the amino derivative. For these reasons and because nucleophilic alkyl phosphites have been used to reduce metal centers,[40,41] it was of interest to explore reactions of **3** with Pt and Pd precursors. The palladium and platinum complexes M(**3**)$_2$Cl$_2$ (**15**, M = Pd; **16**, M = Pt) were easily synthesized from the ligand and the respective M(cod)Cl$_2$ precursors. No evidence for reduction of either Pt or Pd was observed. The ^{31}P{^{1}H} NMR spectrum of the Pd complex, **15**, showed an AA′XX′ spin system characteristic of a trans-structure, but in contrast, the platinum analogue, **16**, did not show any second-order NMR behavior suggesting that **16** has a cis structure. This is the only case in this suite of reactions wherein the final product stereochemistry is different for the Pd and the Pt complexes of the same ligand derived from the same generic metal precursor. The line separation ($|^2J_{\sigma^2P\sigma^4P} + {}^4J_{\sigma^2P\sigma^4P'}|$) for **15** was 51 Hz. In **16** the $^2J_{PP}$ value is directly observable at 58 Hz showing that an increase in this coupling from 25 Hz in the free ligand **3** to ca. 58 Hz has occurred on complex formation. In each complex of ligand **3** the ^{31}P NMR signals for the two-coordinate phosphorus center were shifted downfield by only small amounts. The exo-phosphorus centers were shifted upfield by substantial amounts consistent with expectation upon exocyclic phosphine coordination. The large value of the $^1J_{\sigma^4PPt}$ coupling constant (4811 Hz) recorded for **16** confirms that the exocyclic phosphine is the binding site. The relative magnitudes of the NMR shifts and the general behavior of this trifluoroethoxy ligand indicates a ligand character similar to alkoxyphosphines and also to that of the difluoro analogue **1**, but the reduction chemistry is different, being essentially nonexistent under the reaction conditions.

Summary

The reaction coordination chemistry of the 4-phosphinodiazaphosphole system toward platinum and palladium is quite extensive and complex as a result of the subtle interplay between the properties of the ligands and the metal precursors. For example the difluorophosphine shows a tencency to reduce divalent metal centers to M^0 whereas the bis(dimethylamino) and bis(trifluoroethoxy) derivatives do not. The reduced metal complexes M(**1**)$_4$ (M = Pd, Pt) could be obtained by means of spontaneous reduction processes; however, different precursors were required for Pd (Pd(cod)Cl$_2$) or Pt (Pt(cod)ClMe). Pure reduced Pd(**1**)$_4$ could be formed by appropriate choice of precursor. The initial product of the reaction of **1** with Pt(cod)-ClMe was the disubstitued complex Pt(**1**)$_2$ClMe which however could not be isolated as crystallization induced reduction. The ^{31}P{^{1}H} NMR spectrum for Pt(**1**)$_2$ClMe showed a resonance for each of the exo-phosphorus centers with different values for the one-bond phosphorus−platinum coupling constant consistent with the trans-influence of the methyl and the chloride substituents in the square planar platinum metal center. The facility with which reduction of Pt^{II} occurred with **1** suggests that this ligand may provide some interesting parallels and enhancements of a chemistry similar to PF$_3$ with a much less volatile ligand.

Even though the substitution reactions of **1** tend to proceed without rearrangement of the stereochemistry, **2** gave *trans*-M(**2**)$_2$X$_2$ complexes for all cases investigated perhaps because of the steric bulk at phosphorus in this ligand. The stereochemistry of complexation for the trifluoroethoxy derivative **3** was unusual forming a trans Pd complex but a cis Pt complex from analogous M(cod)Cl$_2$ precursors illustrating, perhaps, the subtle nature of the relationship between ligand and metal steric components. Neither **2** nor **3** showed any propensity for reduction of the metal centers under conditions similar to those wherein **1** produced reduced products.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada and the University of Alberta for support.

Supporting Information Available: Tables of crystallographic details, complete atomic coordinates and *U* values, distances and angles, and anisotropic displacement parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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