

Heterofunctional Ligands Derived from Monooxidized Bis(phosphino)amines. Synthesis and Transition Metal (Rh(I), Pd(II), Pt(II)) Complexes of the Triphosphorus Ligands ((iminophosphoranyl)amino)phosphine Phosphinic Oxides $\text{Ph}_2\text{PN}(\text{R})\text{Ph}_2\text{P}=\text{NP}(\text{O})(\text{OPh})_2$ ($\text{R} = \text{CH}_3, \text{C}_2\text{H}_5$). Crystal and Molecular Structures of the Rhodium(I) and Platinum(II) Complexes $(\text{PhO})_2(\text{O})\text{PN}=\text{PPh}_2\text{N}(\text{C}_2\text{H}_5)\text{Ph}_2\text{PRh}(\text{CO})\text{Cl}$ and $(\text{PhO})_2(\text{O})\text{PN}=\text{PPh}_2\text{N}(\text{C}_2\text{H}_5)\text{Ph}_2\text{PPtCl}_2$

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Oxidation of bis(diphenylphosphino)alkylamines with a phosphinic azide gave ambifunctional triphosphorus ligands of the form $\text{Ph}_2\text{PN}(\text{R})\text{Ph}_2\text{P}=\text{NP}(\text{O})(\text{OPh})_2$ ($\text{R} = \text{CH}_3, \text{C}_2\text{H}_5$). The ^{31}P NMR spectra show large values (ca. 100 Hz) for the couplings between the P^{III} and the adjacent, central, P^{V} and smaller (ca. 40 Hz) couplings between this central P^{V} and the terminal P^{V} . The terminal P^{III} did not show observable coupling to the terminal P^{V} . These ligands complexed readily with Rh(I), Pd(II), or Pt(II) centers. Crystal structures of the rhodium complex $(\text{PhO})_2(\text{O})\text{PN}=\text{PPh}_2\text{N}(\text{C}_2\text{H}_5)\text{Ph}_2\text{PRh}(\text{CO})\text{Cl}\cdot\text{CH}_3\text{CN}$ [at 23 °C, orthorhombic, $Pbca$ (No. 61), $a = 20.277(2)$ Å, $b = 21.860(2)$ Å, $c = 18.498(2)$ Å, $V = 8200(1)$ Å³, $Z = 8$, $R = 0.069$, $R_w = 0.053$] and the platinum complex $(\text{PhO})_2(\text{O})\text{PN}=\text{PPh}_2\text{N}(\text{C}_2\text{H}_5)\text{Ph}_2\text{PPtCl}_2\cdot 2\text{CH}_2\text{Cl}_2$ [at 23 °C, triclinic, $P\bar{1}$ (No. 2), $a = 11.752(3)$ Å, $b = 20.996(4)$ Å, $c = 9.716(2)$ Å, $\alpha = 98.75(2)^\circ$, $\beta = 105.04(2)^\circ$, $\gamma = 99.04(2)^\circ$, $V = 2236(1)$ Å³, $Z = 2$, $R = 0.049$, $R_w = 0.043$] showed that, in both cases, the ligand was coordinated to the metal through the P^{III} and the imine nitrogen to form square planar complexes. The chelate framework structure of the Pt complex was almost planar throughout whereas the Rh complex showed significant puckering of the backbone atoms. For each complex, however, the backbone amine nitrogen is planar and the $\text{P}^{\text{III}}\text{--N--P}^{\text{V}}$ angles are close to 120°. The $\text{P}^{\text{III}}\text{--N}$ bond lengths lie in the single-bond range in both cases, but this bond is notably shorter in the Pt complex (1.70(1) Å) than in the Rh complex (1.777(12) Å). In the Pt complex this latter shortening is accompanied by a notable increase in the $\text{P}^{\text{V}}\text{--amine nitrogen bond}$ (1.67(1) Å versus 1.642(12) Å in the Rh complex) and the $\text{P}^{\text{V}}\text{--imine nitrogen bond}$ (1.67(1) Å versus 1.580(11) Å in the Rh complex), and both of the bonds between the bridging P^{V} and the substituent nitrogen atoms are of identical length. In contrast the Rh complex shows dissimilar $\text{P}^{\text{V}}\text{--N}$ bond lengths toward the two different nitrogen atoms. The differences are in part due to the harder character of the Pt(II) center arising from the presence of two Cl substituents on Pt.

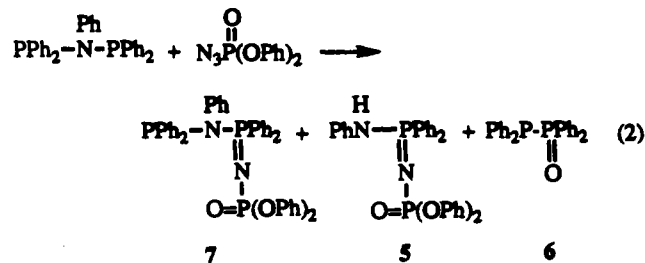
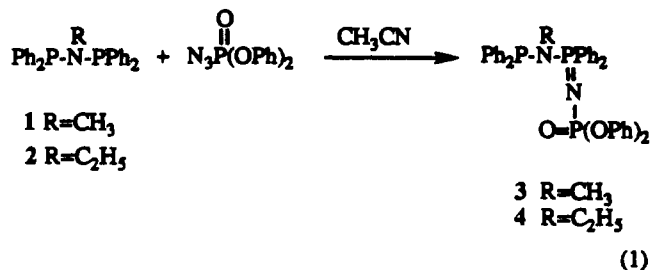
Introduction

We have previously described^{1,2} synthetic, spectroscopic, and structural investigations of coordination compounds of ((iminophosphoranyl)amino)phosphines of the general type $\text{Ph}_2\text{PN}(\text{R})\text{PR}_2(\text{E})$ ($\text{R} = \text{Ph}, \text{Me}, \text{etc.}$; $\text{E} = \text{S}, \text{Se}$; $\text{E} = \text{S}, \text{Se}, \text{NC}_6\text{H}_4\text{-}p\text{-CH}_3, \text{NC}_6\text{F}_4\text{-}p\text{-CN}$). All these ligands readily form chelated complexes with metals.¹⁻³ We report here the synthesis of new, related, potentially trifunctional (or multifunctional) triphosphorus ligands of the type $\text{Ph}_2\text{PN}(\text{R})\text{Ph}_2\text{P}=\text{NR}'$ ($\text{R} = \text{Me}, \text{Et}$; $\text{R}' = \text{NP}(\text{O})(\text{OPh})_2$) which are readily obtained⁴ from the parent bis(phosphino)amine and the phosphinic azide $(\text{PhO})_2\text{P}(\text{O})\text{N}_3$. Coordination compounds of these new ligands with Rh(I), Pd(II), and Pt(II) centers were prepared, and two examples, one Rh(I) and one Pt(II) complex, were structurally characterized.

Results and Discussion

The reactions of bis(phosphino)amines, $\text{Ph}_2\text{PN}(\text{R})\text{PPh}_2$ (**1**, $\text{R} = \text{CH}_3$; **2**, $\text{R} = \text{C}_2\text{H}_5$),⁵ with 1 mol of phosphinic azide in CH_2Cl_2

at -78 °C gave the new nitrogen-bridged ((iminophosphoranyl)amino)phosphinephosphinic oxides $\text{Ph}_2\text{PN}(\text{R})\text{Ph}_2\text{P}=\text{NP}(\text{O})(\text{OPh})_2$ (**3**, $\text{R} = \text{CH}_3$; **4**, $\text{R} = \text{C}_2\text{H}_5$) in good yield (eq 1). Attempts



to prepare the phenylamino analog through reaction of bis(diphenylphosphino)phenylamine with limited quantities of this oxo-phosphinic azide under similar reaction conditions led to the

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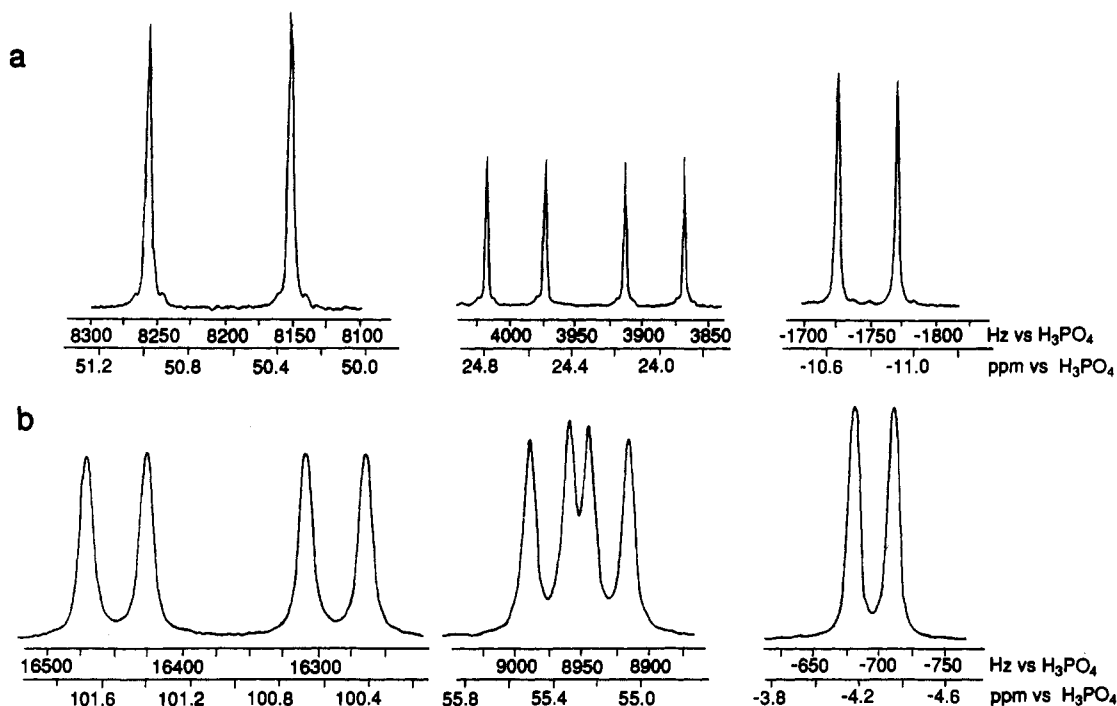


Figure 1. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of (a) compound 4 and (b) the Rh complex of the same ligand (9).

Table 1. Phosphorus-31 NMR Data for Ligands (3, 4) and Their Complexes^a

compd	chem shifts and shift differences, ppm						coupling consts, Hz		
	$\delta(\text{P}^{\text{III}})$	$\Delta\delta^b$	$\delta(\text{P}^{\text{V}})_{[\text{N}]}$	$\Delta\delta$	$\delta(\text{P}^{\text{V}})_{[\text{O}]}$	$\Delta\delta$	$^2J_{\text{PP}[\text{N}]}$	$^2J_{\text{PP}[\text{O}]}$	$^1J_{\text{PM}}$
(PhO) ₂ P(O)N=PPH ₂ N(CH ₃)PPh ₂ (3)	53.9		26.0		-11.0		99.3	41.5	
(PhO) ₂ P(O)N=PPH ₂ N(C ₂ H ₅)PPh ₂ (4)	50.6		24.3		-10.8		105.0	45.0	
(PhO) ₂ P(O)N=PPH ₂ N(CH ₃)PPh ₂ Rh(CO)Cl (8)	100.6	46.7	53.4	27.4	-4.6	6.4	40.5	30.7	163.6
(PhO) ₂ P(O)N=PPH ₂ N(C ₂ H ₅)PPh ₂ Rh(CO)Cl (9)	101.0	50.4	55.3	30.4	-4.3	6.5	45.0	29.0	162.0
(PhO) ₂ P(O)N=PPH ₂ N(CH ₃)PPh ₂ PdCl ₂ (10)	76.6	22.7	60.3	34.3	-5.4	5.6	33.0	29.0	
(PhO) ₂ P(O)N=PPH ₂ N(C ₂ H ₅)PPh ₂ PdCl ₂ (11)	73.2	22.6	56.7	31.8	-6.0	4.8	37.6	26.6	
(PhO) ₂ P(O)N=PPH ₂ N(CH ₃)PPh ₂ PtCl ₂ (12) ^c	50.7	-3.2	61.1	35.1	-6.5	4.5	32.4	25.0	3761.6
(PhO) ₂ P(O)N=PPH ₂ N(C ₂ H ₅)PPh ₂ PtCl ₂ (13) ^c	49.0	-1.6	59.4	34.5	-6.9	3.9	32.9	30.3	3725.0

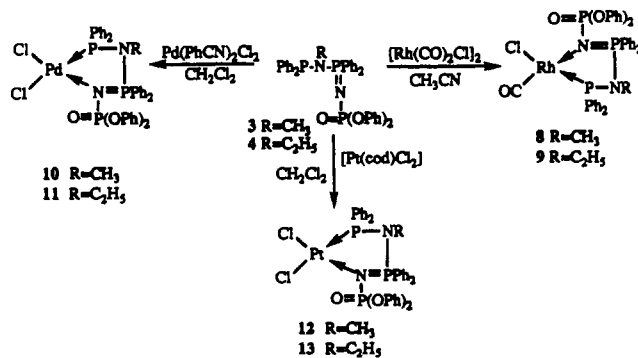
^a All spectra in CDCl_3 or CD_2Cl_2 ; δ ppm vs 85% H_3PO_4 ; coupling constants in Hz. ^b $\Delta\delta = \delta(\text{complex}) - \delta(\text{free ligand})$. ^c Complexes 12 and 13 show $^3J_{\text{P}^{\text{III}}\text{P}^{\text{V}}[\text{O}]}$ coupling (through metal) of 2.5 and 2.2 Hz, respectively.

isolation of major amounts of the acyclic phosphazene 5 along with tetraphenyldiphosphine monoxide 6 and reduced amounts of the desired phosphinophosphinimine 7 as shown in eq 2.⁴ We attribute this result to hydrolytic cleavage of the $\text{P}^{\text{III}}\text{-N}(\text{Ph})$ bond in 7 by water present in the commercial azide. Although pure 7 could be isolated by crystallization, the difficulty of obtaining reasonable quantities of the material inhibited the investigation of its ligand chemistry. We find, however, that the alkylamino bis(phosphines) 1 and 2 are not susceptible to this type of cleavage and the desired phosphinimino aminophosphines 3 and 4 can be easily obtained in good yield from the commercial phosphinic azide. Complexation chemistry therefore focused on these readily obtainable materials.

The ^{31}P NMR spectra of 3 and 4 show three well separated phosphorus signals with equal relative intensities (see Figure 1a). The terminal P^{III} and $\text{P}^{\text{V}}_{[\text{O}]}$ signals were simple doublets each differently coupled to the central $\text{P}^{\text{V}}_{[\text{N}]}$ linkage. The central $\text{P}^{\text{V}}_{[\text{N}]}$ group shows coupling to both kinds of terminal phosphorus and therefore appears as a doublet of doublets in the phosphorus NMR (Table 1).

Reaction of 3 and 4 with Rh(I), Pd(II), and Pt(II) Complexes. The new heterodifunctional ligands 3 and 4 each react with $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ in CH_3CN at 25 °C to give five-membered chelates with the phosphine and the imine nitrogen atoms as donor sites (Scheme 1). The monomeric complexes 8 and 9 are air-stable, crystalline solids.

Scheme 1



The infrared spectra of the complexes show CO absorptions at 1988 and 1987 cm^{-1} , respectively, for 8 and 9 which is clearly consistent with the *cis* related CO/phosphine structure proposed for these complexes. The ^{31}P NMR spectra are diagnostic, particularly in the case of the Rh(I) complexes which show Rh to P^{III} coupling values ($^1J_{\text{RhP}^{\text{III}}}$) of 163.6 and 162.0 Hz for complexes 8 and 9, respectively, which clearly indicate that the phosphine is coordinated to the metal (Figure 1b). The question as to which of the remaining base atoms of the ligand completes the chelate, the imine nitrogen or the phosphoryl oxygen, can also be addressed by the ^{31}P NMR spectra. Complexes 8 and 9

Table 2. Crystal Data for
 $(\text{PhO})_2(\text{O})\text{PN}=\text{PPh}_2\text{N}(\text{C}_2\text{H}_5)\text{Ph}_2\text{PRh}(\text{CO})\text{Cl}\cdot\text{CH}_3\text{CN}$ (**9**) and
 $(\text{PhO})_2(\text{O})\text{PN}=\text{PPh}_2\text{N}(\text{C}_2\text{H}_5)\text{Ph}_2\text{PPtCl}_2\cdot 2\text{CH}_2\text{Cl}_2$ (**13**)

	9	13
formula	$\text{C}_{41}\text{H}_{38}\text{ClN}_3\text{O}_4\text{P}_3\text{Rh}$	$\text{C}_{40}\text{H}_{39}\text{Cl}_2\text{N}_2\text{O}_3\text{P}_3\text{Pt}$
M_r	868.05	1096.49
cryst system	orthorhombic	triclinic
cryst size, mm	$0.400 \times 0.200 \times 0.100$	$0.200 \times 0.040 \times 0.040$
space group	$Pbca$ (No. 61)	$P\bar{1}$ (No. 2)
a , Å	20.277(2)	11.752(3)
b , Å	21.860(2)	20.996(4)
c , Å	18.498(2)	9.716(2)
α , deg		98.75(2)
β , deg		105.04(2)
γ , deg		99.04(2)
V , Å ³	8200(1)	2236(1)
$F(000)$	3552	1084
$\mu(\text{Mo K}\alpha)$, cm ⁻¹	6.32	36.74
D_{calc} , g cm ⁻³	1.406	1.628
Z	8	2
no. of obsd reflns	2130	2681
max 2θ , deg	47.6	45.1
R^a	0.069	0.049
R_w^b	0.053	0.043

$$^a R = \sum \|F_o\| - \|F_c\| / \sum \|F_o\|, \quad ^b R_w = \{\sum w(\|F_o\| - \|F_c\|)^2 / \sum w \|F_o\|^2\}^{1/2}.$$

exhibit three distinct phosphorus signals for the P^{III}, P^V_[N], and P^V_[O] centers upon complexation (Table 1). The chemical shifts of the P^{III} centers are also shifted to lower field by approximately 50 ppm relative to the free ligands. The chemical shift of the P^V_[N] centers is also shifted by 30 ppm to low field relative to the free ligands, whereas the chemical shifts due to the P^V_[O] centers are shifted by only approximately 6 ppm to lower field strongly suggesting that the P^V_[O] center is not involved in the coordination to the metal. This conclusion regarding the species in solution is supported by the X-ray structure of **9** (*vide infra*).

Reactions of **3** and **4** with Cl₂Pd(NCPh)₂ and Pt(cod)Cl₂ in CH₂Cl₂ at 25 °C gave respective chelate complexes **10–13** in good yields. The ³¹P{H}NMR spectra of complexes **10–13** exhibit doublets for both the P^{III} and P^V_[O] centers and either a doublet of doublets (if ²J_{P^{III}P^V_[N]} ≠ ²J_{P^V_[N]P^V_[O]} or a pseudotriplet (if ²J_{P^{III}P^V_[N]} = ²J_{P^V_[N]P^V_[O]}) for the P^V_[N] center. Platinum complexes **12** and **13** showed characteristic, very large, ¹J_{P^{III}Pt} couplings of 3761.6 and 3725 Hz, respectively (therefore P^{III} is coordinated to Pt), but no ²J_{P^{III}P^V} was observed. The Pt complexes **12** and **13** also show very small ³J_{P^{III}MNP^V_[O]} (through metal) couplings of 2.5 and 2.2 Hz, respectively. In contrast similar ³J couplings to the P^{III} center were not observed for the Rh(I) complexes. Relative coordination shifts of the P^V_[O] center also indicate that the imine nitrogen rather than the phosphoryl oxygen binds to the metal. The structure of complex **13**, also established by single-crystal X-ray analysis, is similar to that of the Rh(I) complex, **9**, and again shows that the phosphine and imine nitrogen atoms are the chelating atoms.}}}}}}}

Crystal and Molecular Structures of Complexes 9 and 13. The structures of complexes **9** and **13** were each determined by single-crystal X-ray diffraction studies. Crystal data are given in Table 2. Perspective views of the molecules and the numbering schemes are shown in Figures 2 and 3.⁶ Positional parameters are given in Table 3 and 5, and selected bond lengths and bond angles are listed in Tables 4 and 6, respectively. The rhodium complex **9**,

$(\text{PhO})_2(\text{O})\text{PN}=\text{PPh}_2\text{N}(\text{C}_2\text{H}_5)\text{Ph}_2\text{PRh}(\text{CO})\text{Cl}$, cocrystallized with 1 mol of CH₃CN whereas the platinum complex **13**, $(\text{PhO})_2$ -

$(\text{O})\text{PN}=\text{PPh}_2\text{N}(\text{C}_2\text{H}_5)\text{Ph}_2\text{PPtCl}_2$, cocrystallized with 2 mol of CH₂Cl₂. In complex **9** the rhodium metal lies in an approximately square planar environment, with the $(\text{PhO})_2\text{P}(\text{O})\text{N}=\text{PPh}_2\text{N}(\text{C}_2\text{H}_5)\text{PPh}_2$ ligand connected in a *cis* relationship (*via* the imine

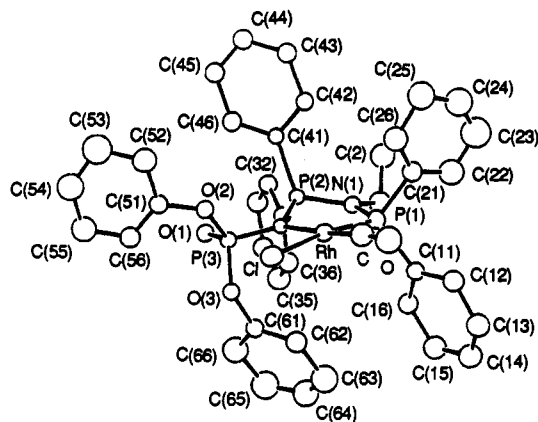


Figure 2. ORTEP⁶ plot of a perspective view of the complex molecule in the crystal structure of $(\text{PhO})_2(\text{O})\text{PN}=\text{PPh}_2\text{N}(\text{C}_2\text{H}_5)\text{Ph}_2\text{PRh}(\text{CO})\text{Cl}\cdot\text{CH}_3\text{CN}$ (**9**) showing the atom-numbering scheme of the complex. Atoms are represented as 20% ellipsoids, and hydrogen atoms have been omitted for clarity.

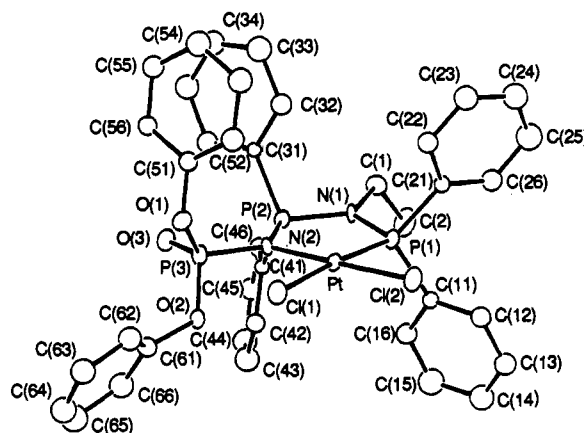


Figure 3. ORTEP⁶ plot of a perspective view of the complex molecule in the crystal structure of $(\text{PhO})_2(\text{O})\text{PN}=\text{PPh}_2\text{N}(\text{C}_2\text{H}_5)\text{Ph}_2\text{PPtCl}_2\cdot 2\text{CH}_2\text{Cl}_2$ (**13**) showing the atom-numbering scheme of the complex. Atoms are represented as 20% ellipsoids, and hydrogen atoms have been omitted for clarity.

nitrogen) and the phosphorus(III) atom to the metal to form a five-membered chelate ring. This central chelate structure is not completely flat. The central square plane defined by the Rh, C (of CO), Cl, N(2), and P(1) atoms deviated from planarity by up to 0.13(2) to $-0.104(4)$ Å. In the backbone, the bridging amine nitrogen N(1) is, within the limits defined by the central plane, also essentially coplanar (0.07 Å) with the central plane. The backbone phosphorus P(2) however lies well out of the plane (0.484 Å) forming the flap of a slightly crinkled envelope. As in previous Rh(I) complex structures of similar heterodifunctional ligands, **9** also shows the carbonyl group to lie in a *cis*-relationship with the phosphine(III) center and the carbonyl group lies *trans* to the more electronegative halogen donor.

The platinum atom in complex **13** lies in the center of a well-defined square planar arrangement of the phosphorus(III), the imine nitrogen, and two chlorine atoms about the metal center. The two chlorine atoms are *cis* as required by the geometry of the bidentate ligand. The entire central framework of the Pt complex including the backbone P(2) and N(1) atoms of the chelate ligand lies very close to planarity; all atoms lie within 0.03(1) Å of the plane defined by the central square plane of Pt, Cl(1), Cl(2), N(2), and P(1) atoms. The bridging phosphorus P(2) lies only about 0.09 Å out of this plane whereas the amine backbone nitrogen, N(1), lies 0.16 Å out of plane again to form the flap of an envelope. All together, however the deviations from central structure planarity are much smaller for the Pt complex than they are for the Rh complex.

(6) Johnson, C. K.; ORTEP; Report ORNL No. 5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

Table 3. Table of Positional Parameters^{a,b} and Thermal Parameters^c of the Central Framework Atoms for

(PhO)₂(O)PN=PPh₂N(C₂H₅)Ph₂PRh(CO)Cl·CH₃CN (9)^d

atom	x	y	z	B, Å ²
Cl	0.1783(2)	0.1781(2)	0.3143(2)	6.2(3)
P(1)	0.3538(2)	0.1608(2)	0.4447(2)	5.0(3)
P(2)	0.2857(2)	0.0522(2)	0.5032(2)	3.5(2)
P(3)	0.1618(2)	0.0703(2)	0.4659(2)	4.0(3)
O	0.3243(7)	0.2548(7)	0.2789(7)	10.5(5)
O(1)	0.1475(5)	0.0237(5)	0.5220(5)	4.6(3)
O(2)	0.1472(5)	0.0439(4)	0.3888(5)	4.6(2)
O(3)	0.1237(5)	0.1358(4)	0.4691(5)	4.2(2)
N(1)	0.3471(6)	0.1009(5)	0.5092(6)	4.1(3)
N(2)	0.2350(6)	0.0933(5)	0.4602(5)	3.1(2)
C	0.3082(9)	0.2159(9)	0.3156(11)	8.0(6)
C(1)	0.3922(9)	0.0958(9)	0.5709(10)	7.4(5)
C(2)	0.4333(10)	0.0403(9)	0.5639(10)	9.2(6)
C(11)	0.3662(8)	0.2371(8)	0.4924(9)	4.8(4)
C(21)	0.4286(9)	0.1433(8)	0.3992(10)	6.2(5)
C(31)	0.2666(8)	0.0309(7)	0.5952(7)	4.3(4)
C(41)	0.3022(7)	-0.0222(7)	0.4552(8)	3.7(4)
C(51)	0.0929(9)	0.0120(8)	0.3670(9)	5.1(4)
C(61)	0.1311(8)	0.1773(8)	0.5282(9)	4.9(4)

^a Estimated standard deviations in parentheses. ^b *ipso* phenyl included; all other phenyl atoms omitted. ^c Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$. ^d Full details for all atoms are given in the supplementary material.

Table 4. Selected Bond Distances and Bond Angles for

(PhO)₂(O)PN=PPh₂N(C₂H₅)Ph₂PRh(CO)Cl (9)

Bond Distances (Å)			
Rh-Cl	2.262(4)	P(2)-C(41)	1.884(15)
Rh-P(1)	2.066(5)	P(3)-O(1)	1.482(10)
Rh-N(2)	2.215(10)	P(3)-O(2)	1.568(10)
Rh-C	1.813(21)	P(3)-O(3)	1.627(10)
P(1)-N(1)	1.777(12)	P(3)-N(2)	1.571(11)
P(1)-C(11)	1.903(16)	O-C	1.17(2)
P(1)-C(21)	1.775(17)	O(2)-C(51)	1.36(2)
P(2)-N(1)	1.642(12)	O(3)-C(61)	1.43(2)
P(2)-N(2)	1.580(11)	N(1)-C(1)	1.47(2)
P(2)-C(31)	1.807(13)	C(1)-C(2)	1.48(2)

Bond Angles (deg)			
Cl-Rh-P(1)	172.0(2)	C(31)-P(2)-C(41)	105.0(7)
Cl-Rh-N(2)	101.6(3)	O(1)-P(3)-O(2)	110.2(6)
Cl-Rh-C	80.5(6)	O(1)-P(3)-O(3)	119.1(6)
P(1)-Rh-N(2)	83.0(3)	O(1)-P(3)-N(2)	117.0(6)
P(1)-Rh-C	95.1(6)	O(2)-P(3)-O(3)	105.5(6)
N(2)-Rh-C	176.7(7)	O(2)-P(3)-N(2)	103.6(6)
Rh-P(1)-N(1)	109.2(5)	O(3)-P(3)-N(2)	99.7(6)
Rh-P(1)-C(11)	111.0(5)	P(3)-O(2)-C(51)	128(1)
Rh-P(1)-C(21)	115.9(7)	P(3)-O(3)-C(61)	122.4(9)
N(1)-P(1)-C(11)	110.1(7)	P(1)-N(1)-P(2)	119.4(7)
N(1)-P(1)-C(21)	103.0(7)	P(1)-N(1)-C(1)	122(1)
C(11)-P(1)-C(21)	107.2(9)	P(2)-N(1)-C(1)	118(1)
N(1)-P(2)-N(2)	99.1(6)	Rh-N(2)-P(2)	120.7(6)
N(1)-P(2)-C(31)	105.4(7)	Rh-N(2)-P(3)	124.4(6)
N(1)-P(2)-C(41)	117.2(7)	P(2)-N(2)-P(3)	113.5(7)
N(2)-P(2)-C(31)	118.8(7)	Rh-C-O	173(2)
N(2)-P(2)-C(41)	111.7(6)	N(1)-C(1)-C(2)	110(2)

In each of the complexes **9** and **13** the backbone amine nitrogen N(1) is planar with P^{III}-N(1)-P^V angles 119.4(7) and 120.2(7)°, respectively. The imine nitrogen, N(2), is also planar. The angles N(2)-Rh-P(1) and N(2)-Pt-P(1) are 83.0(3) and 88.6(3)°, respectively, close to 90°, which suggests that the five-membered chelate rings are relatively strain free. In complex **13** the Pt-Cl(2) bond distance, 2.293(5) Å, which is *trans* to the imine nitrogen, is notably shorter than the Pt-Cl(1) bond distance, 2.364(5) Å *trans* to the coordinating phosphine. In general Pd-Cl or Pt-Cl bond distances decrease as the electronegativity of the *trans* positioned substituent increases. Similar trends have been observed in our previous work and also by others.⁷⁻⁹

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Table 5. Positional Parameters^{a,b} and Thermal Parameters^c of the Central Framework Atoms for

(PhO)₂(O)PN=PPh₂N(C₂H₅)Ph₂PPtCl₂·2CH₂Cl₂ (13)^d

atom	x	y	z	B(eq), Å ²
Pt	0.29035(09)	0.21351(04)	0.08206(08)	2.33(3)
Cl(1)	0.3245(05)	0.2717(02)	0.3223(05)	4.1(2)
Cl(2)	0.2808(05)	0.1185(02)	0.1716(05)	4.3(2)
Cl(3)	0.5663(08)	0.1353(04)	0.5812(08)	12.1(5)
Cl(4)	0.6742(08)	0.1901(04)	0.3861(09)	12.0(5)
Cl(5)	-0.0864(09)	0.2443(04)	0.0334(09)	13.4(6)
Cl(6)	-0.1173(08)	0.1423(05)	0.1846(08)	13.2(5)
P(1)	0.2521(05)	0.1518(02)	-0.1334(05)	2.7(2)
P(2)	0.2839(05)	0.2849(02)	-0.1917(04)	2.6(2)
P(3)	0.3128(05)	0.3726(03)	0.0648(05)	3.1(2)
O(1)	0.4336(11)	0.3909(06)	0.2001(10)	3.6(5)
O(2)	0.2095(11)	0.3689(05)	0.1377(10)	2.8(5)
O(3)	0.3096(11)	0.4171(05)	-0.0382(11)	3.8(5)
N(1)	0.2677(12)	0.2040(06)	-0.2482(12)	2.1(6)
N(2)	0.2947(12)	0.2958(06)	-0.0142(12)	2.1(6)
C(1)	0.2678(18)	0.1796(09)	-0.4007(18)	3.4(9)
C(2)	0.148(02)	0.1452(10)	-0.5076(18)	6(1)
C(3)	0.556(02)	0.1841(12)	0.451(02)	8.4(7)
C(4)	-0.019(03)	0.1857(15)	0.105(03)	10.4(8)
C(11)	0.0987(16)	0.1029(09)	-0.1990(16)	2.7(4)
C(21)	0.3527(16)	0.0973(08)	-0.1519(16)	2.6(4)
C(31)	0.4150(15)	0.3238(08)	-0.2298(15)	2.0(4)
C(41)	0.1509(15)	0.3084(08)	-0.2921(15)	2.1(4)
C(51)	0.5445(19)	0.3885(10)	0.1788(18)	3.5(4)
C(61)	0.1917(19)	0.4233(10)	0.2328(20)	3.8(5)

^a Estimated standard deviations in parentheses. ^b *ipso* phenyl included; all other phenyl atoms omitted. ^c Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$. ^d Full details for all atoms are given in the supplementary material.

Table 6. Selected Bond Distances and Bond Angles for

(PhO)₂(O)PN=PPh₂N(C₂H₅)Ph₂PPtCl₂ (13)

Bond Distances (Å)			
Pt-Cl(1)	2.364(5)	P(2)-C(41)	1.79(2)
Pt-Cl(2)	2.293(5)	P(3)-O(1)	1.61(1)
Pt-P(1)	2.181(5)	P(3)-O(2)	1.56(1)
Pt-N(2)	2.09(1)	P(3)-O(3)	1.47(1)
P(1)-N(1)	1.70(1)	P(3)-N(2)	1.63(1)
P(1)-C(11)	1.82(2)	P(1)-C(51)	1.38(2)
P(1)-C(21)	1.79(2)	O(2)-C(61)	1.44(2)
P(2)-N(1)	1.67(1)	N(1)-C(1)	1.49(2)
P(2)-N(2)	1.67(1)	C(1)-C(2)	1.50(3)
P(2)-C(31)	1.78(2)		

Bond Angles (deg)			
Cl(1)-Pt-Cl(2)	87.7(2)	O(1)-P(3)-O(2)	103.9(6)
Cl(1)-Pt-P(1)	174.8(2)	O(1)-P(3)-O(3)	113.9(7)
Cl(1)-Pt-N(2)	96.3(3)	O(1)-P(3)-N(2)	108.5(7)
Cl(2)-Pt-P(1)	87.4(2)	O(2)-P(3)-O(3)	115.6(7)
Cl(2)-Pt-N(2)	175.9(4)	O(2)-P(3)-N(2)	101.6(7)
P(1)-Pt-N(2)	88.6(3)	O(3)-P(3)-N(2)	112.3(6)
Pt-P(1)-N(1)	106.4(5)	P(3)-O(1)-C(51)	121(1)
Pt-P(1)-C(11)	112.4(5)	P(3)-O(2)-C(61)	124(1)
Pt-P(1)-C(21)	116.0(6)	P(1)-N(1)-P(2)	120.2(7)
N(1)-P(1)-C(11)	108.3(7)	P(1)-N(1)-C(1)	122(1)
N(1)-P(1)-C(21)	105.5(7)	P(2)-N(1)-C(1)	118(1)
C(11)-P(1)-C(21)	107.8(8)	N(1)-P(2)-C(41)	107.4(7)
N(1)-P(2)-N(2)	105.5(6)	Pt-N(2)-P(3)	127.6(6)
N(1)-P(2)-C(31)	106.9(8)	P(2)-N(2)-P(3)	113.9(7)
N(2)-P(2)-C(31)	114.1(7)	Pt-N(2)-P(2)	118.5(7)
N(2)-P(2)-C(41)	111.0(7)	N(1)-C(1)-C(2)	117(2)
C(31)-P(2)-C(41)	111.5(7)		

The P-N bond distances and the central core relationships (compared in Figure 4) in these complexes are of some interest because we might expect the ligands to be essentially identical in these closely related complexes and yet they are different. In

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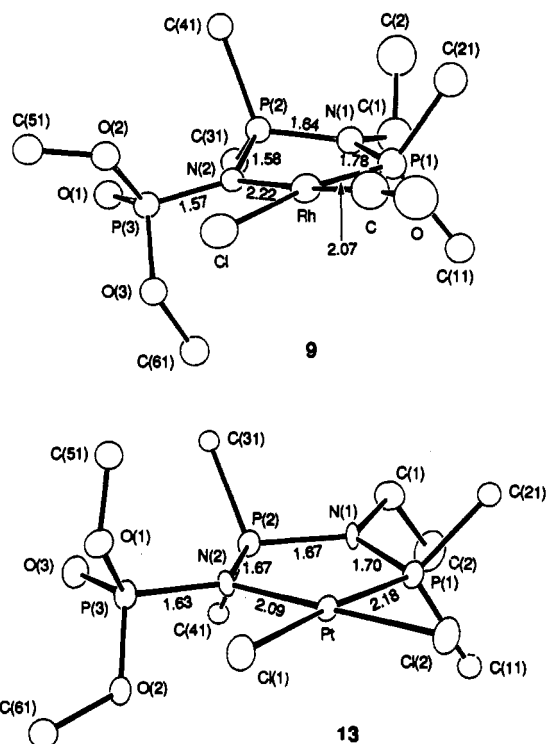


Figure 4. Comparison of the central coordination framework structures of complexes 9 and 13.

complex 9, the backbone P–N bonds show different lengths as would be expected given that the phosphorus and nitrogen atoms individually demonstrate different valence and coordination states. The P(1)–N(1) bond distance of 1.777(12) Å is comparable with the normally accepted single bond value of 1.77 Å, and the P^V(2)–N(1)_{amine} distance of 1.642(7) Å is closer to the value (ca. 1.6 Å) typically associated with P=N bond lengths in cyclic phosphazenes indicating that the P^V(2)–N(1)_{amine} nitrogen has more multiple-bond character than does the P^{III}(1)–N(1)_{amine} nitrogen bond as would be expected. The P^V(2)–N(2)_{imine} bond distance of 1.580(11) Å is notably shorter than a typical P–N double-bond length (1.64 Å),^{10,11} suggesting an even higher bond order. This shortening is notable in both complexes and may be due, in part, to the substantial electron-withdrawing character of the phosphinic oxide substituent on the imine nitrogen. Similarly shortened P^V=N bonds have also been observed in the Cl(CO)Rh–imine complexes of Ph₂PCH₂PPh₂=NC₆F₄-*p*-CN² and Ph₂PC₆H₄PPh₂=NSi(CH₃)₃.¹² The P(3)–N(2) bond is also notably shortened in both 13 (1.63 Å) and especially in 9 (1.57 Å) whereas this is nominally a single bond. This could also be due to the same electron withdrawing effect of the phosphinic oxide substituent.

In contrast to the expected patterns, the backbone of 13 shows essentially equivalent bond lengths between the bridging P^V(2) and both the amine and imine nitrogen atoms (1.67(1) Å in both cases). Even though the shortening of the P^V(3)–N(2) bond length is not as marked as in 9, the value in 13 is typical of a double bond rather than a single bond. These bond length values are suggestive of extensive delocalization in these ligands which in 13 extends throughout the ligand backbone and in 9 is focused on the imine (N(2)) nitrogen.

The Rh–N bond length in 9 of 2.215(10) Å is notably longer than the values we^{2,12} and others have observed for similar bonding in imine–Rh(I)^{13,14} or oxoquinoline–Rh(I)¹⁵ complexes. The Rh–N bond length in 9 is similar to that observed (ca. 2.2 Å) in a collection of cyclic amino–phosphine–Rh(I) complexes wherein

an amine nitrogen is bound to Rh(I).¹⁶ It is also notable that the metal–nitrogen, N(2), bond length in 9 is substantially longer than the corresponding distance in 13. This lengthening is accompanied by a shortening of the bond between the P^{III} and the metal such that the P^{III}–M bond length is substantially longer in 13 than in 9. We suggest that the differences arise from the difference in hard/soft character of the metal centers. The two very electronegative Cl substituents on Pt enhance its hard character and in turn increase its propensity for binding to the hard atom, nitrogen. The metal–nitrogen bond is therefore relatively short, and the metal–phosphorus bond is relatively long. In contrast the CO ligand enhances the softness of the Rh center with the result that the Rh binds better to the softer phosphorus(III) than to nitrogen and the reverse pattern of ligand atom binding is displayed. The anticipated stronger binding of the imine nitrogen is counteracted by the change in the character of the metal atom with the result that the nitrogen binding is weaker as in an amine. This reduced binding between the Rh and nitrogen however leads to an enhancement of the binding between this imine nitrogen and the adjacent phosphorus atoms which is revealed by the shortening of both P(3)–N(2) and P(2)–N(2) in 9. Likewise the enhancement of Rh–P binding reduces the bond order between P(1) and N(1) and this bond length increases.

Conclusion

Potentially multifunctional phosphorus ligands are easily obtained *via* single-stage oxidation of bis(diphenylphosphino)alkylamines with the phosphinic azide (PhO)₂P(O)N₃. These ligands act as bifunctional chelates toward Rh(I), Pd(II), and Pt(II) centers, coordinating through the P^{III} and the imine nitrogen centers. Crystal structures of the Rh and Pt complexes verify the coordination behavior and show square planar environments about each metal. The backbone structures of the ligands are different in the two cases as the result of the different character of the metal centers.

Experimental Section

All experimental manipulations were performed under an atmosphere of dry argon. Solvents were dried and distilled prior to use. Ph₂PN(Me)PPh₂,⁵ Ph₂PN(Et)PPh₂,⁵ [Rh(CO)₂Cl]₂,¹⁷ [PdCl₂(NCPPh₂)₂],¹⁸ and [Pt(cod)Cl]₂¹⁹ were prepared according to published procedures or minor modifications thereof. ¹H and ³¹P NMR spectra were recorded on a Bruker WH 400 instrument operating at the appropriate frequencies using tetramethylsilane and 85% H₃PO₄ as internal and external references, respectively. CDCl₃ and CD₂Cl₂ were used as both solvent and the internal lock. Positive shifts lie downfield in all cases. Infrared spectra were recorded on a 20SX Nicolet FT IR instrument in CH₂Cl₂ solution. Microanalyses were obtained in this department.

Synthesis of (PhO)₂P(O)N=PPh₂N(R)PPh₂ (3, R = Me; 4, R = Et). A solution of N₃P(O)(OPh)₂ (11 mmol) in CH₂Cl₂ (25 mL) was added dropwise to a stirred solution of Ph₂PN(R)PPh₂ (R = Me (1) or Et (2)) (10 mmol) also in CH₂Cl₂ (30 mL) at –78 °C. The mixture was then warmed to room temperature, and stirring was continued for a further 4 h. The solvent was then removed under vacuum to give the analytically pure, crystalline, products 3 or 4.

(PhO)₂P(O)N=PPh₂N(CH₃)PPh₂ (3). Yield: 78%. Mp: 46–48 °C. Anal. Calcd for C₃₇H₃₃N₂O₃P₃: C, 68.73; H, 5.11; N, 4.33. Found: C, 68.25; H, 5.06; N, 4.29. IR (CH₂Cl₂): ν(P=N) 1310 cm⁻¹. ¹H NMR (CD₂Cl₂): phenyl rings, 7.30, 7.70 (m, 30H); –NCH₃, 2.68 (d, 3H, ³J_{P–H} = 5.0, ³J_{P–H} = 0 Hz). ³¹P{¹H} NMR (CDCl₃): δ(P^{III}), 53.9 (d); δ(P^V)_N, 26.0 (dd); δ(P^V)_O, –11.0 (d); J_{P^{III}P^V(N)}} = 99.3 Hz, ²J_{P^V(O)P^V(N)}} = 41.5 Hz.

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(PhO)₂P(O)N=PPh₂N(C₂H₅)PPh₂ (4). Yield: 92%. Mp: 104 °C. Anal. Calcd for C₃₈H₃₅N₂O₃P₃: C, 69.09; H, 5.30; N, 4.24. Found: C, 68.70; H, 5.28; N, 4.24. IR (CH₂Cl₂): ν(P=N) 1308 cm⁻¹. ¹H NMR (CD₂Cl₂): phenyl rings, 7.18, 7.40, 7.55, 7.82 (m, 30H); NCH₂, 3.6 (m, 2H); C-CH₃, 0.38 (t, 3H, ³J_{HH} = 7 Hz). ³¹P{¹H} NMR (CD₂Cl₂): δ(P^{III}), 50.6 (d); δ(P^V)_N, 24.3 (dd); δ(P^V)_O, -10.8 (d), ²J_{PMPV(N)} = 105.0 Hz, ²J_{PV(N)PV(O)}} = 45.0 Hz.

Synthesis of (PhO)₂(O)PN=PPh₂N(R)Ph₂PRh(CO)Cl (8, R = CH₃; 9, R = C₂H₅). A solution of 3 or 4 (2 mmol) in dry CH₃CN (15 mL) was added dropwise to a stirred solution of [Rh(CO)₂Cl]₂ (1 mmol) in the same solvent (15 mL) at 25 °C. After the completion of the addition, the mixture was stirred for 3 h. The clear yellow solution was concentrated (to 12 mL) and cooled to 0 °C to give yellow crystals of 8 or 9 in good yield.

8. Pale yellow crystals formed. Yield: 84%. Mp: 92 °C dec. Anal. Calcd for C₃₈H₃₃ClN₂O₄P₃Rh: C, 56.12; H, 4.06; N, 3.44. Found: C, 56.02; H, 3.99; N, 3.32. IR (CH₂Cl₂): ν(CO) 1988 cm⁻¹; ν(P=N) 1250 cm⁻¹. ¹H NMR (CD₂Cl₂): phenyl rings, 7.18, 7.36, 7.65 (m, 30H); NCH₃, 2.44 (dd, 3H, ³J_{PH} = 11.0, 6.0 Hz). ³¹P{¹H} NMR (CD₂Cl₂): δ(P^{III}), 100.6 (dd, ¹J_{PRh} = 163.6 Hz, ²J_{PMPV(N)} = 40.5 Hz); δ(P^V)_N, 53.4 (dd, ²J_{PMPV(N)} = 40.5 Hz; ²J_{PV(N)PV(O)}} = 30.7 Hz); δ(P^V)_O, -4.6 (d, ²J_{PV(O)PV(N)}} = 30.7 Hz).

9. Bright yellow crystals formed. Yield: 88%. Mp: 150 °C dec. Anal. Calcd for C₄₁H₃₈ClN₂O₄P₃Rh: C, 56.71; H, 4.38; N, 4.84. Found: C, 56.42; H, 4.39; N, 5.06. IR (CH₂Cl₂): ν(CO) 1987 cm⁻¹; ν(P=N) 1250 cm⁻¹. ¹H NMR (CD₂Cl₂): phenyl rings, 7.15, 7.55, 7.73 (m, 30H); -NCH₂, 2.95 (m, 2H). C-CH₃, 0.55 (t, 3H, ³J_{HH} = 7.0 Hz). ³¹P{¹H} NMR (CD₂Cl₂): δ(P^{III}), 101.0 (dd, ¹J_{PRh} = 162.0 Hz; ²J_{PMPV(N)} = 45.0 Hz); δ(P^V)_N, 55.3 (dd, ²J_{PV(N)Pm} = 45.0 Hz; ²J_{PV(N)PV(O)}} = 29.0 Hz); δ(P^V)_O, -4.3 (d, ²J_{PV(N)PV(O)}} = 29.0 Hz).

Synthesis of (PhO)₂(O)PN=PPh₂N(R)Ph₂PPdCl₂ (10, R = CH₃; 11, R = C₂H₅). A solution of 3 or 4 (ca. 1 mmol) in CH₂Cl₂ (ca. 15 mL) was added dropwise to a solution of [PdCl₂(NCPH₂)₂] (ca. 1 mmol) also in CH₂Cl₂ (ca. 15 mL) with stirring at 25 °C; the stirring was continued for 3 h before the solution was concentrated to 8 mL, diluted with 3 mL hexane, and cooled to 0 °C to give as crystalline products 10 or 11.

10. Yellow crystals formed. Yield: 72%. Mp: 148 °C dec. Anal. Calcd for C₃₈H₃₃Cl₄N₂O₃P₃Pd: C, 50.19; H, 3.85; N, 3.08. Found: C, 49.19, H, 3.64; N, 3.05. IR (CH₂Cl₂): ν(P=N) 1245 cm⁻¹. ¹H NMR (CD₂Cl₂): phenyl rings, 7.20, 7.55, 7.75 (m, 30H), NCH₃, 2.38 (dd, 3H, ³J_{PH} = 22.0, 14.0 Hz). ³¹P{¹H} NMR (CD₂Cl₂): δ(P^{III}), 76.6 (d, ²J_{PMPV(N)} = 33.0 Hz); δ(P^V)_N, 60.3 (br) (not resolved); δ(P^V)_O, -5.4 (d, ²J_{PV(N)PV(O)}} = 29.0 Hz).

11. Pale yellow crystals formed. Yield: 74%. Mp: 173 °C dec. Anal. Calcd for C₃₉H₃₇Cl₄N₂O₃P₃Pd: C, 50.73; H, 4.01; N, 3.04. Found: C, 50.45; H, 3.79; N, 3.11. IR (CH₂Cl₂): ν(P=N) 1260 cm⁻¹. ¹H NMR (CD₂Cl₂): phenyl rings, 7.15, 7.55, 7.82 (m, 30H); -NCH₂, 2.90 (m, 2H); -CH₃, 0.64 (t, 3H, ³J_{HH} = 6.0 Hz). ³¹P{¹H} (CD₂Cl₂): δ(P^{III}), 73.2 (d); δ(P^V)_N, 56.7 (dd); δ(P^V)_O, -6.0 (d); ²J_{PMPV(N)}, 37.6 Hz; ²J_{PV(N)PV(O)}} = 26.6 Hz.

Synthesis of (PhO)₂(O)PN=PPh₂N(R)Ph₂PPtCl₂ (12, R = CH₃; 13, R = C₂H₅). A solution of 3 or 4 (ca. 1 mmol) in CH₂Cl₂ (ca. 15 mL) was added dropwise to a solution of [Pt(cod)Cl₂] (ca. 1 mmol) in the same solvent (ca. 15 mL) with stirring at 25 °C. Stirring was continued for 4 h. The clear yellow solution was concentrated to 8 mL, 3 mL of hexane was added, and the solution was cooled to 0 °C to give crystals of 12 or 13 in good yield.

12. Light yellow crystals formed. Yield: 80%. Mp: 120–122 °C. Anal. Calcd for C₃₇H₃₃Cl₃N₂O₃P₃Pt: C, 48.68; H, 3.61; N, 3.07. Found: C, 48.36; H, 3.67; N, 2.89. IR (CH₂Cl₂): ν(P=N) 1250 cm⁻¹. ¹H NMR (CD₂Cl₂): phenyl rings, 7.20, 7.50, 7.70 (M, 30H); NCH₃, 2.42 (dd, 3H, ³J_{PH} = 9.0; 6.0 Hz). ³¹P{¹H} NMR (CD₂Cl₂): δ(P^{III}), 50.7 (dd); δ(P^V)_N, 61.1 (t, ²J_{PV(N)Pm} = 32.4 Hz); δ(P^V)_O, -6.5 (dd). ¹J_{PmPm} = 3761.6 Hz; ²J_{PMPV(N)} = 32.4 Hz; ²J_{PMPV(O)}} = 2.5 Hz, ²J_{PmPm} not observed.

13. Yellow-green crystals formed. Yield: 82%. Mp: 206 °C dec. Anal. Calcd for C₄₀H₃₉Cl₃N₂O₃P₃Pt: C, 43.79; H, 3.55; N, 2.55. Found: C, 43.67; H, 3.42; N, 2.50. IR (CH₂Cl₂): ν(P=N) 1255 cm⁻¹. ¹H NMR (CD₂Cl₂): phenyl rings, 7.06, 7.40, 7.70 (M, 30H); -NCH₂, 2.90 (m, 2H); -CH₃, 0.50 (t, 3H, ³J_{HH} = 7.0 Hz). ³¹P{¹H} NMR (CD₂Cl₂): δ(P^{III}), 49.0 (dd); δ(P^V)_N, 59.4 (dd); δ(P^V)_O, -6.9 (dd); ¹J_{PmPm} = 3725 Hz; ²J_{PMPV(N)} = 32.9 Hz; ²J_{PmPm} = 30.3 Hz; ²J_{PMPV(O)}} = 2.2 Hz, ²J_{PmPm} not observed.

X-ray Structure Determinations. The structures of the two compounds (PhO)₂(O)PN=PPh₂N(C₂H₅)Ph₂PRh(CO)Cl·CH₃CN (9) and (PhO)₂(O)PN=PPh₂N(C₂H₅)Ph₂PPtCl₂·2CH₂Cl₂ (13) were determined by X-ray diffraction. The crystallographic and data collection parameters are summarized in Table 2. In both cases, suitable single crystals (obtained from CH₃CN solution in the case of 9 and from a 2:1 mixture of CH₂Cl₂ and hexane in the case of 13) were mounted on glass fibers and the measurements were made on a Rigaku AFC6R diffractometer at the Molecular Structure Corp., College Station, TX, with graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å) and a 12-kW rotating anode generator. Unit cell dimensions (Table 2) were determined by least squares refinement of the best angular positions for 25 (in the case of 9) and 6 (in the case of 13) carefully centered reflections in the range 22.43 < 2θ < 31.20° for 9 and 20.44 < 2θ < 23.48° for 13. The data points were collected at ±1 °C using the ω-2θ scan technique. The intensities of 3 standard reflections were remeasured after every 150 reflections. They remained constant throughout the data collection in the case of 9 indicating crystal and electronic stability so corrections for decomposition were deemed unnecessary. However, in the case of 13, the intensities declined by 48.0%. A linear correction factor was applied to the latter data to correct for this decrease. All data were corrected for Lorentz, polarization, and background effects (also for absorption in the case of compound 13). After removal of redundant and space group forbidden data, the remaining observed data with I ≥ 3.0σ(I) were used for solution and refinement. Neutral-atom scattering factors were taken from Cromer and Waber.²⁰ Anomalous dispersion effects were included²¹ in F_c; the values given by Δf' and Δf'' were those given by Cromer.²²

The structures were solved by direct methods.^{23,24} The non-hydrogen atoms were refined either anisotropically or isotropically. Hydrogen atoms were calculated on idealized positions and included in the refinement as sliding atoms with fixed isotropic thermal parameters. All calculations were done using the TEXSAN package of programs.²⁵

Complete listings of positional parameters, bond distances and angles, anisotropic thermal parameters, and plane analyses for 9 and 13 are provided as supplementary material.

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Supplementary Material Available: For (PhO)₂(O)PN=PPh₂N(C₂H₅)Ph₂PRh(CO)Cl·CH₃CN (9), Table S1, atomic coordinates and B_{eq} values for all non-hydrogen atoms, Table S2, hydrogen atom coordinates and B_{eq} values, Table S3, all non-hydrogen bond lengths, Table S4, intramolecular bond angles involving the non-hydrogen atoms, Table S5, intramolecular distances involving the hydrogen atoms, Table S6, intramolecular bond angles involving the hydrogen atoms, Table S7, torsion angles, Table S8, least-squares planes, and Table S9, anisotropic displacement parameters for central atoms, and for (PhO)₂(O)PN=PPh₂N(C₂H₅)Ph₂PPtCl₂·2CH₂Cl₂ (13), Table S10, atomic coordinates and B_{eq} values for all non-hydrogen atoms, Table S11, non-hydrogen bond lengths, Table S12, intramolecular bond angles involving the non-hydrogen atoms, Table S13, torsion angles, Table S14, least-squares planes, and Table S15, anisotropic displacement parameters for central atoms (27 pages). Ordering information is given on any current masthead page.

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