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New 10-Membered Inorganic Heterocyclic Diphosphanes, $PhN(PX)_2\{(-OC_6H_2(^tBu)_2)(\mu\text{-}S)((^tBu)_2C_6H_2O-)\}$ (X = Cl, F). Synthesis and Transition Metal Complexes (Molybdenum(0), Ruthenium(II), Palladium(II), and Platinum(II)) of Heterocyclic Diphosphanes. Crystal and Molecular Structures of the Chloro Derivative, $PhN(PCl)_2\{(-OC_6H_2(^tBu)_2)(\mu\text{-}S)((^tBu)_2C_6H_2O-)\}$, and of a Molybdenum(0) Complex of the Fluoro Derivative, $[Mo(CO)_3\{\eta^3\text{-}PhN(PF)_2\{(-OC_6H_2(^tBu)_2)(\mu\text{-}S)((^tBu)_2C_6H_2O-)\}\text{-}\kappa P,\kappa P,\kappa S\}]$

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Bis(dichlorophosphino)aniline, $PhN(PCl_2)_2$, reacts with stoichiometric amounts of 2,2′-thiobis(4,6-di-*tert*-butylphenol) to afford a 10-membered heterocycle, $PhN(PCl)_2\{(-OC_6H_2(^tBu)_2)(\mu\text{-}S)((^tBu)_2C_6H_2O-)\}$ (**1**), in high yield. The structure of the heterocycle has been determined by a single-crystal X-ray analysis. The 10-membered heterocycle **1** reacts with SbF_3 to afford the corresponding fluoro derivative **2** in good yield. The compounds **1** and **2** act as tridentate ligands with molybdenum carbonyl derivatives, forming complexes of the type $[Mo(CO)_3\{\eta^3\text{-}PhN(PX)_2\{(-OC_6H_2(^tBu)_2)(\mu\text{-}S)((^tBu)_2C_6H_2O-)\}\text{-}\kappa P,\kappa P,\kappa S\}]$ (**3** X = Cl, **4** X = F). A crystal structure of the fluoro derivative **4** showed the facial tricarbonyl complex comprising a relatively strain-free tetracyclic structure with molybdenum in an octahedral environment; the two phosphorus and the sulfur centers were the donor atoms. Compound **2** readily reacts with Ru(II), Pd(II), and Pt(II) derivatives to form chelate complexes, demonstrating the η^2 mode of coordination.

Introduction

Heterocyclic ring systems containing trivalent phosphorus atoms are distinguished from the open-chain phosphorus compounds by some special characteristics not evident in the latter.[1−3] One of the most important features is the rigid stereochemistry at the phosphorus centers in the ring. Also, it is the ring substituents and the different functionalities at the phosphorus centers that make the heterocycles fascinating with respect to both structural and electronic properties. Heterocycles with P−C, P−N, P−O, and P−S bonds, in addition to their great biochemical and commercial importance,[4] play a major role in some substitution mechanisms as intermediates or as transition states.[5−7] Also, some phosphorus-containing heterocycles have been found to be potentially carcinostatic[8,9] among other pharmacological activities. The introduction of tervalent phosphorus centers into the ring enhances the versatility of the heterocycles in complexing with both hard and soft metals. Since the tervalent phosphorus centers can stabilize transition metals in low oxidation states, such complexes can be potential homogeneous or phase-transfer catalysts in various organic transformations. As a part of our interest[10−16] and the interest of others[17−20] in designing new types of cyclic and acyclic phosphorus-based ligands, we now report the synthesis of the 10-membered inorganic heterocycles with five heteroatoms

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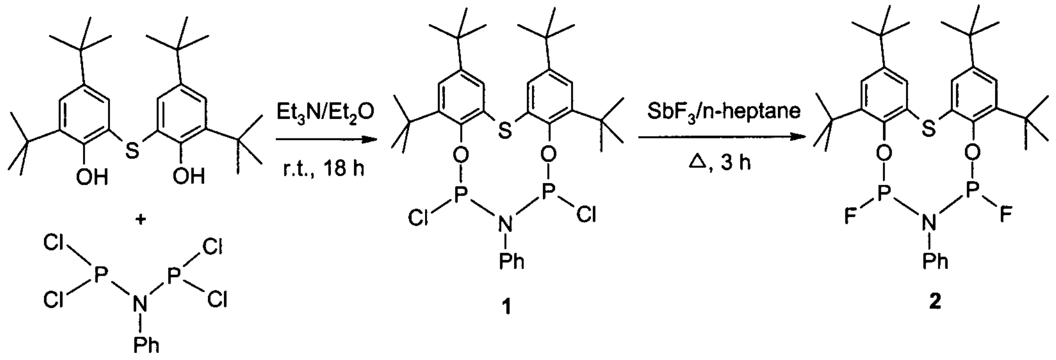
Scheme 1



in the ring, PhN(PX)$_2${(−OC$_6$H$_2$(^{t}Bu)$_2$)(μ-S)((^{t}Bu)$_2$C$_6$H$_2$O−)} (**1** X = Cl, **2** X = F), their spectroscopic characterization, and the X-ray structure analysis of **1**. Transition metal chemistry of **1** and **2** is also described. Compound **1** retains the P−Cl bond during the complex formation and exhibits η^2 and η^3 modes of coordination by utilizing a third donor atom such as sulfur. The X-ray structure of a tricarbonyl molybdenum(0) complex with the fluoro derivative acting as a tridentate ligand, [Mo(CO)$_3${η^3-PhN(PF)$_2${(−OC$_6$H$_2$(^{t}Bu)$_2$)(μ-S)((^{t}Bu)$_2$C$_6$H$_2$-O−)}-κP,κP,κS}], is also reported. The structure provides a rare example of a phosphane heterocycle showing the flexible tridentate (η^3) coordination despite the presence of sterically crowded substituents on the phosphorus centers.

Results and Discussion

The stoichiometric reaction of bis(dichlorophosphino)aniline, Cl$_2$PN(Ph)PCl$_2$, with 2,2′-thiobis(4,6-di-*tert*-butylphenol) in diethyl ether at ambient temperature afforded the thermodynamically favored 10-membered heterocycle, PhN(PCl)$_2${(−OC$_6$H$_2$(^{t}Bu)$_2$)(μ-S)((^{t}Bu)$_2$C$_6$H$_2$O−)} (**1**), in 89% yield (Scheme 1).

The heterocyclic diphosphane **1** is a highly crystalline, white solid that is soluble in dichloromethane, chloroform, toluene, acetone, and acetonitrile and is moderately stable in air and in moisture. The new 10-membered heterocycle represents the first of its kind with five different elements and with coordinating properties as well. The confirmation of the structure and molecular composition of the heterocycle comes from NMR spectroscopy (^{1}H, ^{31}P), high-resolution mass spectrometry, and elemental analysis. The ^{31}P NMR spectrum of **1** shows a single resonance at 145.7 ppm indicating that the two phosphorus centers are equivalent. The molecular structure is further confirmed by X-ray crystallography.

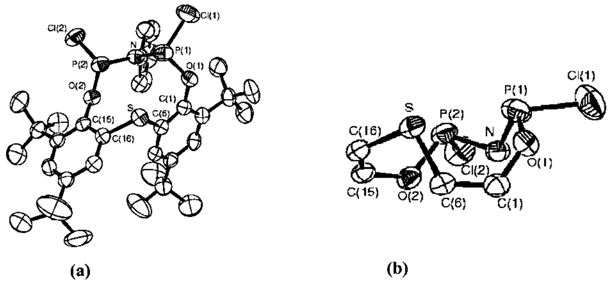


Figure 1. (a) Perspective view of **1** showing the atom numbering scheme. Thermal ellipsoids are drawn at the 50% probability level and hydrogen atoms are omitted for clarity. (b) View of the heterocyclic ring displaying only the core atoms.

Table 1. Crystal Data for **1** and **4**

	1	**4**
formula	$C_{34}H_{45}Cl_2NO_2P_2S$	$C_{37}H_{45}F_2MoNO_5P_2S$
mol wt	664.61	811.69
a, Å	9.8492(8)	11.7037(7)
b, Å	17.6284(19)	12.2971(5)
c, Å	21.2737(17)	16.5033(8)
α, °		102.382(4)
β, °	102.918(6)	98.894(5)
γ, °		114.284(4)
V, Å^3	3600.2(6)	2034.5(2)
Z	4	2
space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No.2)
temp, K	293	293
λ (Mo Kα),^{a} Å	0.71073	0.71073
ρ_{calcd}, g cm^{-3}	1.226	1.325
μ (Mo Kα), cm^{-1}	0.4	0.5
R^b	0.0516	0.0420
$R_{w2}{}^c$	0.1268	0.1270
wgt par *a*, *b*^{c}	0.076, 0.330	0.07, 0.339

^{a} Graphite monochromated. ^{b} $R = \sum|F_o - F_c|/\sum F_o|$. ^{c} $R_{w2} = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$; $P = 1/3[F_o^2 + 2F_c^2]$.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for PhN(PCl)$_2${(−OC$_6$H$_2$(*t*Bu)$_2$)(μ-S)((*t*Bu)$_2$C$_6$H$_2$O−)} (**1**)

bond distances (Å)		bond angles (°)	
P(1)−N	1.691(3)	P(1)−N−P(2)	109.16(18)
P(2)−N	1.718(3)	P(1)−N−C(29)	127.6(3)
N−C(29)	1.459(5)	P(2)−N−C(29)	123.1(3)
P(1)−Cl(1)	2.067(19)	P(1)−O(1)−C(1)	126.9(2)
P(2)−Cl(2)	2.074(17)	P(2)−O(2)−C(15)	122.0(2)
S−C(16)	1.773(4)	O(1)−P(1)−N	104.12(15)
S−C(6)	1.782(4)	O(2)−P(2)−N	101.48(15)
P(1)−O(1)	1.636(3)	Cl(1)−P(1)−N	103.12(13)
P(2)−O(2)	1.631(3)	Cl(2)−P(2)−N	97.94(12)
O(1)−C(1)	1.398(5)	Cl(1)−P(1)−O(1)	95.29(12)
O(1)−C(15)	1.403(4)	Cl(2)−P(2)−O(2)	96.73(11)
C(15)−C(16)	1.403(5)	C(6)−S−C(16)	101.02(18)

The structure of PhN(PCl)$_2${(−OC$_6$H$_2$(^{t}Bu)$_2$)(μ-S)((^{t}Bu)$_2$-C$_6$H$_2$O−)} (**1**) with the atom numbering scheme is shown in Figure 1. Crystal data and selected bond lengths and bond angles are given in Tables 1 and 2, respectively. The structure consists of a 10-membered ring puckered in a cuplike shape in such a way that the lone pairs on the phosphorus centers and the two chlorine atoms are remote from the bulky aryloxy groups. The two chlorine atoms are mutually cis and are located on the same side of the ring. The P(1)−N−P(2) bond angle of 109.15(18)° is larger than the average P−N−P bond angles (97°−100°) observed in cyclodiphosphazanes.[21−24] The bond angles around the nitrogen sum to 355.77°, indicating that the planar geometry

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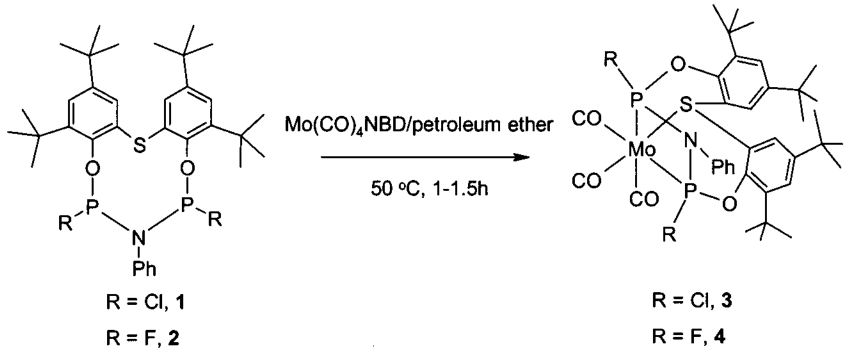
Scheme 2



around the amine nitrogen is retained. The P(1)−N (1.691(3) Å) bond is slightly shorter than the P(2)−N (1.718(3) Å) bond. A single ^{31}P NMR resonance in solution suggests that the observed difference may result from packing or from other solid-state effects. The average P−N bond length of 1.704(3) Å is shorter than the normally accepted value for a single bond (1.77 Å),[25] but it compares well with those found in a variety of phosphorus(III)−nitrogen compounds[26] suggesting a degree of P−N multiple bonding. The P−O (mean) bond distance of 1.633(3) Å is larger than the average P−O bond distance of 1.600(6) Å observed in $[\{PhNP\}_2\{-O(CH_2)_3O-\}]$,[23] while the P··P nonbonded separation is 2.778 Å.

The reaction of cyclic phosphorochloridite **1** with SbF_3 affords the fluoro derivative $PhN(PF)_2\{(-OC_6H_2(^tBu)_2)(\mu\text{-}S)((^tBu)_2C_6H_2O-)\}$ (**2**) in good yield (Scheme 1). The identification of the fluoro derivative **2** is based on mass spectrometry, elemental analysis, and NMR spectroscopic data. The ^{31}P NMR spectrum of compound **2** consists of XAA′X′ doublets with $|^1J_{PF} + {}^3J_{PF}| = 1153$ Hz. The ^{31}P NMR spectrum of **2** is best interpreted as the A part of the XAA′X′ nuclear spin system[27] with $J_{XX'} = 0$.

The 10-membered heterocycles **1** and **2** with three potential donor atoms (two tervalent phosphorus centers and a sulfur center) can act as 2e$^-$ (η^1), 4e$^-$ (η^2 or μ), or 6e$^-$ (η^3) donors depending upon the metal reagents, the stoichiometry, and the reaction conditions. The reactions of **1** and **2** with [Mo(CO)$_4$NBD] in petroleum ether afford the tricarbonyl derivatives, $[Mo(CO)_3\{\eta^3\text{-}PhN(PX)_2\{(-OC_6H_2(^tBu)_2)(\mu\text{-}S)((^tBu)_2C_6H_2O-)\}\text{-}\kappa P,\kappa P,\kappa S\}]$ (**3** X = Cl, **4** X = F), by the displacement of a coordinated olefin and a carbonyl group with ligands **1** and **2**, respectively, exhibiting a tridentate mode of coordination as shown in Scheme 2.

The infrared spectra of complexes **3** and **4** exhibit strong absorptions in the range 1890−1987 cm^{-1} characteristic of phosphine donors bound to [M(CO)$_3$] moiety in the *facial* conformation.[28,29] The ^{31}P NMR spectra of complexes **3** and **4** exhibit single resonances which are shielded compared to those of the free ligands. The coordination shift is around 10 ppm. The fluoro derivative shows phosphorus−fluorine couplings similar to those in the free ligand. Further evidence for the molecular composition of complexes **3** and **4** comes from the elemental analysis, mass spectrometry, and the single-crystal X-ray structure determination of the fluoro derivative **4**.

The structure of the molybdenum complex, $[Mo(CO)_3\{\eta^3\text{-}PhN(PF)_2\{(-OC_6H_2(^tBu)_2)(\mu\text{-}S)((^tBu)_2C_6H_2O-)\}\text{-}\kappa P,\kappa P,\kappa S\}]$ (**4**), is confirmed by a single-crystal X-ray diffraction study. Crystal data are given in Table 1, a perspective view of the molecule with the numbering scheme is shown in Figure 2, and selected bond lengths and bond angles are listed in Table 3. The structure of **4** shows a monomeric chelated metal complex with a typical octahedral metal environment in which the fluoro ligand acts as a tridentate ligand via two tervalent phosphorus and one sulfur centers in a *facial* orientation. The ligand is puckered in such a way that the sulfur atom and one of the phosphorus centers along with the two carbonyl groups occupy the equatorial positions. The remaining carbonyl group and the other phosphorus center are in the axial positions. The S−Mo−P(2) and S−Mo−P(1) bond angles are 81.66(4)° and 79.98(4)°, respectively. There is no significant difference in the equatorial and axial Mo−C bond lengths; the average Mo−C bond length is 2.004(2) Å. The mean P−N bond length is 1.690(3) Å. The P(1)−N−P(2) bond angle (98.8°) is considerably smaller than

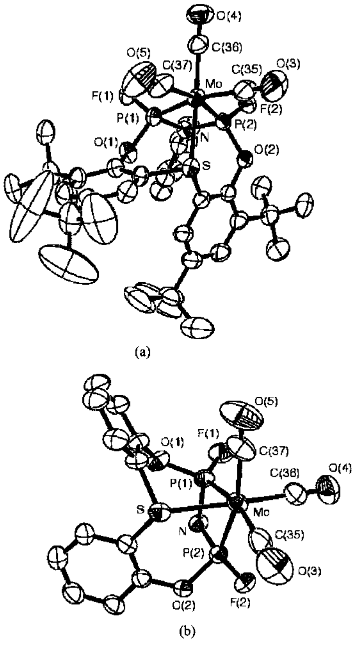


Figure 2. (a) Perspective view of **4** showing the atom numbering scheme. Thermal ellipsoids are drawn at the 50% probability level and hydrogen atoms are omitted for clarity. (b) Plot of the central core of **4**.

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Scheme 3

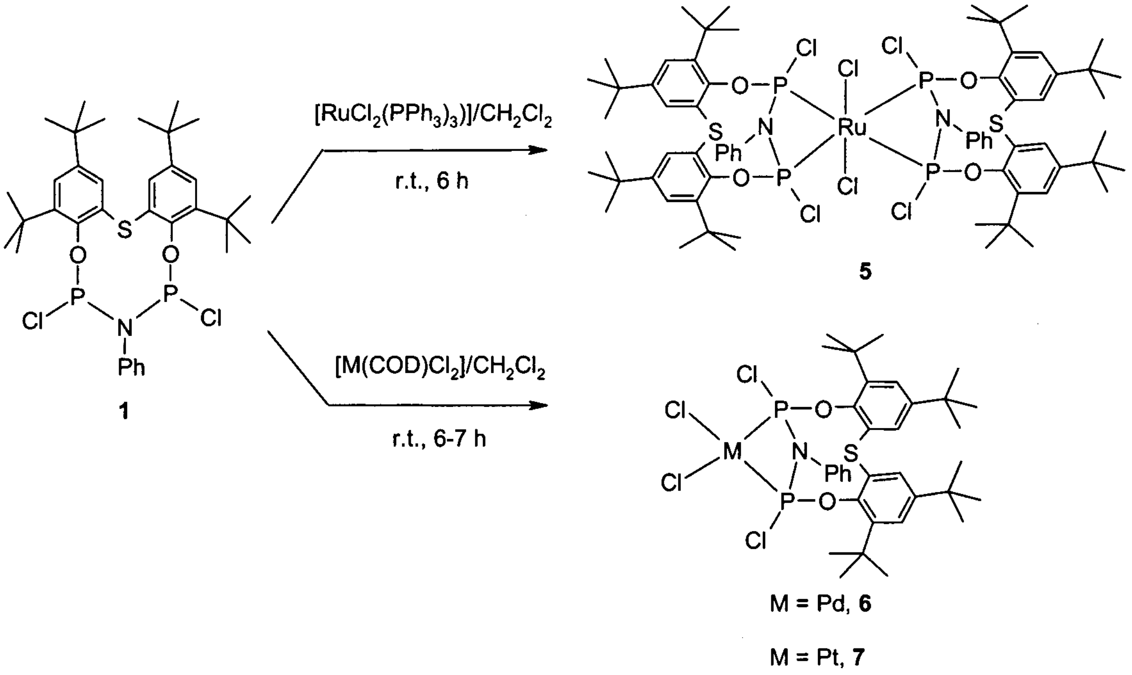

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for [Mo(CO)$_3${η^3-PhN(PF)$_2${(−OC$_6$H$_2$(^{t}Bu)$_2$)(μ-S)((^{t}Bu)$_2$C$_6$H$_2$O−)}-κP,κP,κS}] (**4**)

bond distances (Å)		bond angles (°)	
Mo−S	2.5242(1)	S−Mo−P(1)	79.98(4)
Mo−P(1)	2.3770(12)	S−Mo−P(2)	81.66(4)
Mo−P(2)	2.3653(12)	C(36)−Mo−C(37)	91.3(2)
Mo−C(35)	2.000(5)	C(35)−Mo−C(36)	89.7(2)
Mo−C(36)	1.9977(5)	P(1)−Mo−C(37)	101.50(14)
Mo−C(37)	2.015(5)	P(2)−Mo−C(35)	98.32(14)
S−C(2)	1.789(4)	S−Mo−C(37)	89.18(14)
S−C(20)	1.808(4)	S−Mo−C(35)	93.82(14)
P(1)−F(1)	1.585(3)	S−Mo−C(36)	176.41(15)
P(2)−F(2)	1.568(3)	P(1)−Mo−C(35)	163.16(14)
P(1)−O(1)	1.618(3)	P(2)−Mo−C(37)	165.09(14)
P(2)−O(2)	1.617(3)	O(1)−P(1)−Mo	122.51(11)
P(1)−N	1.693(3)	O(2)−P(2)−Mo	119.89(11)
P(2)−N	1.682(3)	N−P(1)−Mo	97.51(12)
		N−P(2)−Mo	98.28(12)
		P(1)−N−P(2)	98.8(2)
		P(1)−N−C(29)	129.7(2)
		P(2)−N−C(29)	131.4(2)
		P(1)−Mo−P(2)	65.42(4)

either tetrahedral or trigonal angles, but the sum of the angles around the nitrogen is 359.9° which clearly indicates that the geometry around the nitrogen is planar. The decrease in the P(1)−N−P(2) bond angle is a consequence of chelation.

The reaction of **1** with [RuCl$_2$(PPh$_3$)$_3$] in a 2:1 ratio in CH$_2$Cl$_2$ solution affords an octahedral complex, *trans*-[Ru(Cl)$_2${η^2-PhN(PCl)$_2${(−OC$_6$H$_2$(^{t}Bu)$_2$)(μ-S)((^{t}Bu)$_2$C$_6$H$_2$O−)}-κP,κP}$_2$] (**5**), in 93% yield (Scheme 3). The ^{31}P NMR spectrum shows a single resonance at 122.7 ppm, indicating that all of the PPh$_3$ ligands have been replaced by two phosphane heterocycles, with each one acting as a bidentate chelating ligand. The ^{1}H NMR spectrum and the microanalysis of complex **5** agree well with the proposed molecular composition. Treatment of [M(COD)-Cl$_2$] (M = Pd or Pt) with 1:1 molar proportions of compound **1** in CH$_2$Cl$_2$ affords the chelate complexes **6** and **7** in good yield (Scheme 3). In both of the complexes, the heterocyclic diphosphane ligand exhibits a chelating bidentate mode of coordination via two phosphorus centers.

The ^{31}P NMR spectrum of palladium complex **6** exhibits a single resonance at 74.5 ppm indicating the symmetric nature of the molecule. The ^{31}P NMR spectrum of the platinum(II) analogue **7** also exhibits a single resonance at 46.7 ppm which is considerably shielded, as expected, as compared to that of the palladium(II) complex. Also, the platinum(II) complex **7** showed characteristic, very large, $^1J_{\mathrm{PtP}}$ coupling of 4544 Hz that is consistent with the proposed *cis* geometry.[30,31]

Conclusion

Bis(dichlorophosphino)aniline, PhN(PCl$_2$)$_2$, with a PNP backbone reacts with 2,2′-thiobis(4,6-di-*tert*-butylphenol) to form a heterocyclic phosphorochloridite with three potential soft donor centers. The chloro derivative on treatment with SbF$_3$ gives the corresponding fluoro derivative in good yield. The new cyclophosphanes readily form chelate complexes with the platinum metals. Synthetic flexibility, easy synthetic methodology with readily accessible nucleophilic sites, and the presence of three potential donor atoms in this heterocycle are interesting.

Experimental Section

All experimental manipulations were performed under an atmosphere of dry nitrogen using Schlenk techniques.[32] Solvents were dried and distilled prior to use. 2,2′-Thiobis(4,6-di-*tert*-butylphenol),[33] bis(dichlorophosphino)aniline,[34] [Mo(CO)$_4$NBD],[35] [RuCl$_2$(PPh$_3$)$_3$],[36] [Pd(COD)-Cl$_2$],[37] and [Pt(COD)Cl$_2$][38] were prepared according to the published procedures. ^{1}H and ^{31}P{^{1}H} NMR (δ in ppm) spectra were recorded on a VXR 300S spectrometer (operating at the frequencies of 300 and 121 MHz respectively) using TMS and 85% H$_3$PO$_4$, respectively, as external standards. CDCl$_3$ was used both as a solvent and as an internal

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lock. Positive shifts lie downfield of the standard in all of the cases. Infrared spectra were recorded on a Nicolet Impact 400 FTIR instrument in Nujol mull. Microanalyses were performed on a Carlo Erba model 1106 elemental analyzer. Melting points were recorded in capillary tubes and are uncorrected.

Synthesis of $PhN(PCl)_2\{(-OC_6H_2(^tBu)_2)(\mu\text{-}S)((^tBu)_2C_6H_2O-)\}$ (1). A mixture of 2,2′-thiobis(4,6-di-*tert*-butylphenol) (6.9 g, 15.6 mmol) and triethylamine (3.24 g, 32 mmol) in Et_2O (150 mL) was added dropwise to a suspension of bis(dichlorophosphino)aniline (4.6 g, 15.6 mmol) also in Et_2O (100 mL) with vigorous stirring at 0 °C. The mixture was stirred for 18 h at 25 °C. Triethylamine hydrochloride was removed by filtration, and the solvent was removed under reduced pressure to give a white crystalline product of **1** which was recrystallized from a mixture of hexane/dichloromethane (1:1). Yield: 89% (9.24 g). Mp: 183 °C (dec). Anal. Calcd for $C_{34}H_{45}Cl_2NO_2P_2S$: C, 61.52; H, 6.83; N, 2.11. Found: C, 61.48; H, 6.78; N, 2.09. ^1H NMR (300 MHz, $CDCl_3$): δ 7.35 (d, 2H, Ar), 7.11−7.21 (m, 5H, N-phenyl), 7.05(d, 2H, Ar), 1.13 (s, 18H, *tert*-butyl), 1.21 (s, 18H, *tert*-butyl). $^{31}P\{^1H\}$ NMR (121.421 MHz, $CDCl_3$): δ 145.7 (s). HRMS calcd for $C_{34}H_{45}Cl_2NO_2P_2S$ (M^+), 663.2023; found, 663.1998.

Synthesis of $PhN(PF)_2\{(-OC_6H_2(^tBu)_2)(\mu\text{-}S)((^tBu)_2C_6H_2O-)\}$ (2). A mixture of **1** (2 g, 3.0 mmol) and SbF_3 (1.34 g, 7.5 mmol) was heated to reflux in *n*-heptane (100 mL) for 3 h. It was then cooled to room temperature, filtered, and the filtrate was concentrated to 40 mL under reduced pressure. Cooling this solution to 0 °C gave **2** as an analytically pure, white crystalline solid. Yield: 84% (1.6 g). Mp: 180 °C (dec). Anal. Calcd for $C_{34}H_{45}F_2NO_2P_2S$: C, 64.63; H, 7.18; N, 2.21. Found: C, 64.54; H, 7.15; N, 2.19. ^1H NMR (300 MHz, $CDCl_3$): δ 7.41 (d, 2H, Ar), 7.15−7.25 (m, 5H, N-phenyl), 7.11 (d, 2H, Ar), 1.15 (s, 18H, *tert*-butyl), 1.22 (s, 18H, *tert*-butyl). $^{31}P\{^1H\}$ NMR (121.421 MHz, $CDCl_3$): δ 134.7 (m), $|^1J_{PF} + {}^3J_{PF}| = 1153$ Hz. HRMS calcd for $C_{34}H_{45}F_2NO_2P_2S$ (M^+), 631.2614; found, 631.2591.

Synthesis of $[Mo(CO)_3\{\eta^3\text{-}PhN(PCl)_2\{(-OC_6H_2(^tBu)_2)(\mu\text{-}S)((^tBu)_2C_6H_2O\text{-})\}\text{-}\kappa P,\kappa P,\kappa S\}]$ (3). A petroleum ether (8 mL) solution of $[Mo(CO)_4NBD]$ (0.087 g, 0.29 mmol) was added to a suspension of **1** (0.193 g, 0.29 mmol) also in petroleum ether (10 mL). The mixture was heated to 55 °C for 1.5 h to get a clear yellow solution which was allowed to come to room temperature and then filtered. The filtrate was concentrated to 5 mL and was cooled to −20 °C to give **3** as analytically pure, yellowish-green crystals. Yield: 73% (0.18 g). Mp: 160 °C (dec). Anal. Calcd for $C_{37}H_{45}Cl_2MoNO_5P_2S$: C, 52.62; H, 5.37; N, 1.65. Found: C, 52.56; H, 5.33; N, 1.59. IR (Nujol, ν_{CO}, cm^{-1}): 1982 s, 1912 s, 1895 s. ^1H NMR (300 MHz, $CDCl_3$): δ 7.32 (d, 2H, Ar), 7.10−7.19 (m, 5H, N-phenyl), 7.02 (d, 2H, Ar), 1.14 (s, 18H, *tert*-butyl), 1.20 (s, 18H, *tert*-butyl). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$): δ 138.1 (s). MS (FAB, *m/z*) 844.

Synthesis of $[Mo(CO)_3\{\eta^3\text{-}PhN(PF)_2\{(-OC_6H_2(^tBu)_2)(\mu\text{-}S)((^tBu)_2C_6H_2O-)\}\text{-}\kappa P,\kappa P,\kappa S\}]$ (4). A solution of $[Mo(CO)_4NBD]$ (0.087 g, 0.29 mmol) in petroleum ether (5 mL) was added dropwise to a suspension of **2** (0.183 g, 0.29 mmol) also in petroleum ether (5 mL). The mixture was heated to 50−55 °C for 1 h, after which the deep brown solution was allowed to come to room temperature and was then filtered. The filtrate was concentrated to 3 mL and when cooled to −20 °C, it gave **4** as analytically pure, yellowish-green crystals. Yield: 64% (0.15 g). Mp: 155 °C (dec). Anal. Calcd for $C_{37}H_{45}F_2MoNO_5P_2S$: C, 54.75; H, 5.58; N, 1.72. Found: C, 54.63; H, 5.55; N, 1.69. IR (Nujol, ν_{CO}, cm^{-1}): 1987 s, 1918 s, 1894 s. ^1H NMR (300 MHz, $CDCl_3$): δ 7.38 (d, 2H, Ar), 7.12−7.22 (m, 5H, N-phenyl), 7.09 (d, 2H, Ar), 1.11 (s, 18H, *tert*-butyl), 1.21 (s, 18H, *tert*-butyl). $^{31}P\{^1H\}$ NMR (121.421 MHz, $CDCl_3$): δ 132.1 (m), $|^1J_{PF} + {}^3J_{PF}| = 1116$ Hz. MS (FAB, *m/z*) 811.

Synthesis of $[RuCl_2\{\eta^2\text{-}PhN(PCl)_2\{(-OC_6H_2(^tBu)_2)(\mu\text{-}S)((^tBu)_2C_6H_2O-)\}\text{-}\kappa P,\kappa P\}_2]$ (5). A solution of the ligand **1** (0.067 g, 0.1 mmol) in CH_2Cl_2 (8 mL) was added dropwise to a solution of $[RuCl_2(PPh_3)_3]$ (0.048 g, 0.05 mmol) also in CH_2Cl_2 (8 mL). The reaction mixture was stirred for 6 h at 25 °C, and then the solvent was removed under reduced pressure to yield a pale yellow residue. Free PPh_3 was removed by extraction with several aliquots of Et_2O to give an analytically pure, yellow crystalline product of **5**. Yield: 93% (0.07 g). Mp: 230 °C (dec). Anal. Calcd for $C_{68}H_{90}Cl_6N_2O_4P_4RuS_2$: C, 54.39; H, 6.04; N, 1.86. Found: C, 54.60; H, 6.07; N, 1.80. ^1H NMR (300 MHz, $CDCl_3$): δ 7.32 (d, 2H, Ar), 7.08−7.18 (m, 5H, N-phenyl), 7.03 (d, 2H, Ar), 1.03 (s, 18H, *tert*-butyl), 1.18 (s, 18H, *tert*-butyl). $^{31}P\{^1H\}$ NMR (121.421 MHz, $CDCl_3$): δ 122.7(s).

Synthesis of $[PdCl_2\{\eta^2\text{-}PhN(PCl)_2\{(-OC_6H_2(^tBu)_2)(\mu\text{-}S)((^tBu)_2C_6H_2O-)\}\text{-}\kappa P,\kappa P\}]$ (6). A CH_2Cl_2 (5 mL) solution of the ligand **1** (0.18 g, 0.27 mmol) was added dropwise to a solution of $[Pd(COD)Cl_2]$ (0.076 g, 0.27 mmol) also in CH_2Cl_2 (5 mL) at 25 °C. The reaction mixture was stirred for 6 h to give a clear orange-yellow solution which was concentrated to 3 mL and diluted with 1 mL of hexane. After the solution was left to stand at room temperature, **6** formed as an analytically pure, yellow crystalline product. Yield: 76% (0.17 g). Mp: 140−142 °C. Anal. Calcd for $C_{34}H_{45}Cl_4NO_2P_2PdS$: C, 48.50; H, 5.39; N, 1.66. Found: C, 48.32; H, 5.24; N, 1.59. ^1H NMR (300 MHz, $CDCl_3$): δ 7.32 (d, 2H, Ar), 7.12−7.25 (m, 5H, N-phenyl), 7.08 (d, 2H, Ar), 1.05 (s, 18H, *tert*-butyl), 1.23 (s, 18H, *tert*-butyl). $^{31}P\{^1H\}$ NMR (121.421 MHz, $CDCl_3$): δ 74.5 (s).

Synthesis of $[PtCl_2\{\eta^2\text{-}PhN(PCl)_2\{(-OC_6H_2(^tBu)_2)(\mu\text{-}S)((^tBu)_2C_6H_2O-)\}\text{-}\kappa P,\kappa P\}]$ (7). A CH_2Cl_2 (5 mL) solution of the ligand **1** (0.14 g, 0.21 mmol) was added dropwise to a solution of $[Pt(COD)Cl_2]$ (0.078 g, 0.21 mmol) also in CH_2Cl_2 (5 mL) at 25 °C. The reaction mixture was stirred for 7 h to give a clear pale yellow solution. The solution was concentrated to 3 mL, diluted with 1 mL of *n*-hexane, and cooled to 0 °C whereupon an analytically pure sample of **7** precipitated out. Yield: 72% (0.14 g). Mp: 150−152 °C. Anal. Calcd for $C_{34}H_{45}Cl_4NO_2P_2PtS$: C, 43.90; H, 4.88; N, 1.50. Found: C, 43.80; H, 4.81; N, 1.45. ^1H NMR (300 MHz, $CDCl_3$): δ 7.29 (d, 2H, Ar), 7.07−7.18 (m, 5H, N-phenyl), 7.03 (d, 2H, Ar), 1.01 (s, 18H, *tert*-butyl), 1.23 (s, 18H, *tert*-butyl). $^{31}P\ \{^1H\}$ NMR (121.421 MHz, $CDCl_3$): δ 46.7(s), $^1J_{PtP} = 4544$ Hz.

X-ray Crystallography. Crystals of compounds **1** and **4** obtained as described above were mounted on Pyrex filaments with epoxy resin. General procedures for crystal alignment, unit cell determination, and refinement and collection of data on the Enraf-Nonius CAD-4 diffractometer have been published,[39] while details specific to the present study are presented in Table 1. The raw intensity data were corrected for Lorentz and polarization effects, for decreases in the intensities of the monitor reflections,[40] and, in the case of **4**, for absorption using ψ scans[41] on several reflections with χ near 90°. For **1**, the space group was uniquely determined by the systematic absences observed in the final data set, while for **4**, the choice was made on the basis of intensity statistics. Direct methods provided locations for a significant number of atoms in **1**, while the molybdenum atom in **4** was located from a sharpened Patterson function. The completion and refinement of both of the structures were accomplished with successive cycles of difference Fourier syntheses followed by full-matrix, least-squares refinement. As is evident in Figure 2a, two of the *tert*-butyl groups appear to suffer from a degree of positional disorder, but this could not be satisfactorily resolved into separate alternate locations for the methyl carbon atoms. Hydrogen atoms were placed in calculated positions riding on the attached carbon atoms with isotropic displacement parameters 20% larger than those of the attached atom. All calculations associated with structure solution and refinement were performed with the SHELXTL-PLUS[42] program package.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determination of $PhN(PCl)_2\{(-OC_6H_2$-$(^tBu)_2)(\mu$-$S)((^tBu)_2C_6H_2O-)\}$(**1**) and $[Mo(CO)_3\{\eta^3$-$\{PhN(PF)_2\{(-OC_6H_2$-$(^tBu)_2)(\mu$-$S)((^tBu)_2C_6H_2O-)\}$-$\kappa P,\kappa P,\kappa S\}]$ (**4**). This material is available free of charge via the Internet at http://pubs.acs.org.

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