

Transition Metal Chemistry of Main Group Hydrazides. 5.¹ Functionalization of Methylhydrazine With Alkyl/Alkoxy Groups and Aryl/Aryloxy-Substituted Phosphorus(V) Oxides and Sulfides. First Examples of Bidentate Interactions of R₂P(E)(NMeNH₂) (R = OMe, OEt, OPh, Ph; E = S, O) with Pd(II). X-ray Structure of (MeO)₂P(S)NMeNH₂·PdCl₂

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The reactions of alkoxy-, aryloxy-, and aryl-substituted phosphorus monochlorides (R₂P(E)Cl: R = OCH₃, E = S; R = OC₂H₅, E = S; R = OC₆H₅, E = O; R = C₆H₅, E = O) with methyl hydrazine yielded the new monophosphorus hydrazides (R₂P(E)NMeNH₂: R = OCH₃, E = S (1); R = OC₂H₅, E = S (2), R = OC₆H₅, E = O (3); R = C₆H₅, E = O (4)) in good yields. The monophosphorus hydrazides 1–4 reacted smoothly with PdCl₂(PhCN)₂ at 25 °C to give the new cyclopalladaphosphohydrazides R₂P(E)NMeNH₂·PdCl₂ (R = OCH₃, E = S (5); R = OC₂H₅, E = S (6); R = OC₆H₅, E = O (7); R = C₆H₅, E = O (8)) in good yields as air-stable crystalline solids. The chemical constitutions of 1–4 and 5–8 were established by complete NMR (¹H and ³¹P) spectroscopic and C, H, N, and Cl analysis data. The structure of 5 was further confirmed by X-ray diffraction study. Crystal data for 5: monoclinic, space group C2/c, with *a* = 25.029(9) Å, *b* = 10.2800(10) Å, *c* = 9.167(3) Å, β = 104.750(10)°, and Z = 8. The structure was solved by direct methods and was refined to *R* = 0.035.

Introduction

There is considerable current interest in the coordination chemistry of transition metals with the hydrazine family of ligands, stimulated primarily by the versatile bonding modes shown by this class of ligands with both the "electron rich" and "electron poor" transition metals.^{2–4} Although hydrazine frameworks with a variety of organic substituents on one or both the nitrogens have been described in the literature, there is a scarcity of hydrazines with main group functionalities in their backbone. We reasoned that the introduction of additional main group functionalities such as >P(S) or >P(O) on the hydrazine backbone may provide a new approach to the substitutional chemistry of hydrazines. Furthermore, hydrazines functionalized with the main group units (e.g., P(S) or P(O)) in addition to the nitrogen hard bases can be used in heteroatomic chelation of a variety of transition metals. The transition metal chemistry of hydrazines functionalized with main group backbones not only is of fundamental importance in understanding the organometallic

and coordination chemistries of hydrazine ligands but also may enhance the scope and the subsequent utility of hydrazines in transition metal chemistry.

As part of our on going effort in understanding the fundamental transition metal chemistry of main group hydrazides,^{5,6} we recently demonstrated the utility of such main group functionalized hydrazines as novel chelating agents as outlined in Scheme 1. The reactions described in Scheme 1 represent a new development in the use of hydrazine-based ligands for interactions with transition metals. We report herein synthesis of new monophosphorus hydrazides R₂P(E)NMeNH₂ (R = OCH₃, E = S (1); R = OC₂H₅, E = S (2); R = OC₆H₅, E = O (3); R = C₆H₅, E = O, (4)) (Scheme 2). The ligating properties of 1–4 with Pd(II) have been studied. The formation of metallacyclic compounds R₂P(E)NMeNH₂·PdCl₂ (R = OCH₃, E = S (5); R = OC₂H₅, E = S (6); R = OC₆H₅, E = O (7); R = C₆H₅, E = O (8)) and discussion of the X-ray structure of a representative Pd(II) complex, 5, are presented.

Experimental Section

Nuclear magnetic resonance spectra were recorded on a Bruker AMX500 spectrometer. The ¹H NMR chemical shifts are reported in parts per million (ppm) downfield from external standard SiMe₄. The ³¹P NMR spectra were recorded with 85% H₃PO₄ as an external standard, and positive shifts lie downfield of the standard. Infrared spectra were obtained using Nujol mulls and KBr cells on a Mattson Galaxy 3000 spectrometer. Mass spectra (*m/e*) were obtained on a Kratos MS-25 spectrometer. All solvents were freshly distilled reagent grade, and all melting points are uncorrected.

All reactions were performed under anaerobic conditions using nitrogen and conventional Schlenk techniques. Reagents such as (Ph)₂P(O)Cl, (PhO)₂P(O)Cl, (MeO)₂P(S)Cl, and PdCl₂ were purchased from Aldrich Chemical Co. and were used without further purification.

Synthesis of 1-Methylphosphorohydrazidothioic Acid, *O,O*-Dimethyl Ester (1), 1-Methylphosphorohydrazidothioic Acid, *O,O*-Diethyl Ester, (2), 1-Methylphosphorohydrazidic Acid, Diphenyl Ester (3), and Diphenylphosphinic 1-Methylhydrazide (4). A solution of methylhydrazine

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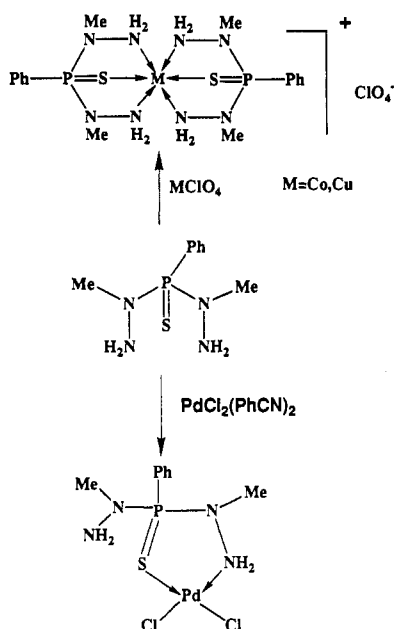
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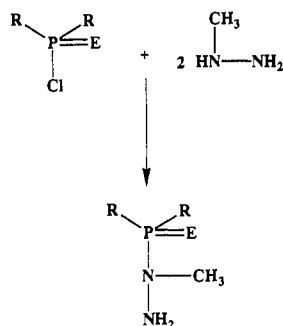
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Scheme 1



Scheme 2



R	E	Compound
OMe	S	1
OEt	S	2
OPh	O	3
Ph	O	4

(75 mmol) in CHCl_3 (75 mL) was added dropwise to a solution of the respective phosphorus chloride (30 mmol) also in 75 mL of CHCl_3 maintained at 0°C . The reaction mixture was stirred for 6 h at 25°C before the methylhydrazine hydrochloride adduct was filtered off and the filtrate evaporated to dryness *in vacuo*. Compound 1 yielded a mixture of products and required separation by flash chromatography. This was achieved by using silica gel 60 as the stationary phase and a solvent system comprised of hexane-ethyl acetate-methanol in the ratio 9:3:1. Compounds 2-4 were recrystallized in CH_3CN to obtain the pure monophosphorus hydrazides.

(CH_3O) $_2\text{P}(\text{S})\text{NMeNH}_2$ (1): oil, yield 80% MS: (M^+) 170. ^{31}P NMR (CDCl_3): 81.5 (s). ^1H NMR (CDCl_3): 3.72 (d, $J = 13.5$ Hz, 6H, P-OCH $_3$), 2.94 (d, 10.8 Hz, N-CH $_3$), 3.61 (s, 2H, NH $_2$). Anal. Calcd for $\text{C}_3\text{H}_{11}\text{N}_2\text{O}_2\text{PS}$: C, 21.12; H, 6.52; N, 16.47. Found: C, 21.09; H, 6.51; N, 16.45.

($\text{C}_2\text{H}_5\text{O}$) $_2\text{P}(\text{S})\text{NMeNH}_2$ (2): oil, yield 91%. ^{31}P NMR (CDCl_3): 77.88 (s). ^1H NMR (CDCl_3): 1.18 (t, 6H, P-OCH $_2\text{CH}_3$), 2.78 (d, $J = 8.1$ Hz, 3H, N-CH $_3$), 3.47 (s, 2H, NH $_2$), 3.97 (m, 4H, P-OCH $_2\text{CH}_3$). Anal. Calcd for $\text{C}_5\text{H}_{15}\text{N}_2\text{O}_2\text{PS}$: C, 30.30; H, 7.63; N, 14.14. Found: C, 30.29; H, 7.62; N, 14.13.

($\text{C}_6\text{H}_5\text{O}$) $_2\text{P}(\text{O})\text{NMeNH}_2$ (3): yellow powder, yield 89%, mp 41°C . ^{31}P NMR (CDCl_3): 0.294. ^1H NMR (CDCl_3): 2.87 (d, $J = 7.8$ Hz, 3H, N-CH $_3$), 3.52 (s, 2H, NH $_2$), 7.1-7.4 (m, 10H, OPh). Anal. Calcd for $\text{C}_{13}\text{H}_{15}\text{N}_2\text{O}_3\text{P}$: C, 56.11; H, 5.43; N, 10.07. Found: C, 56.09; H, 5.42; N, 10.05.

(C_6H_5) $_2\text{P}(\text{O})\text{NMeNH}_2$ (4): white powder, yield 90%, mp 121°C . ^{31}P NMR (CDCl_3): 29.2. ^1H NMR (CDCl_3): 2.62 (d, $J = 8.7$ Hz, 3H,

Table 1. Crystallographic Data for (OMe) $_2\text{P}(\text{S})\text{NMeNH}_2\text{PdCl}_2$ (5)

$a = 25.029(9)$ Å	space group = monoclinic ($C2/c$)
$b = 10.280(1)$ Å	$T = 22(1)^\circ\text{C}$
$c = 9.167(3)$ Å	$\lambda = 0.70930$ Å
$\beta = 104.750(10)^\circ$	$\rho_{\text{calcd}} = 2.018$ g cm $^{-3}$
$V = 2280.9(11)$ Å 3	$\mu = 23.6$ cm $^{-1}$
$Z = 8$	$R^a = 0.035$
fw = 346.56	$R_w^b = 0.054$

$$^a R = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}, \quad ^b R_w = \left[\frac{\sum w(|F_o| - |F_c|)^2}{\sum w|F_o|^2} \right]^{1/2}$$

N-CH $_3$), 3.48 (s, 2H, NH $_2$), 7.5-7.9 (m, 10H, -Ph). Anal. Calcd for $\text{C}_{13}\text{H}_{15}\text{N}_2\text{OP}$: C, 63.41; H, 6.14; N, 11.38. Found: C, 63.40; H, 6.13; N, 11.36.

Synthesis of Compounds $\text{R}_2\text{P}(\text{E})\text{NMeNH}_2\text{PdCl}_2$ ($\text{R} = \text{OCH}_3$, $\text{E} = \text{S}$ (5); $\text{R} = \text{OC}_2\text{H}_5$, $\text{E} = \text{S}$ (6); $\text{R} = \text{OC}_6\text{H}_5$, $\text{E} = \text{O}$ (7); $\text{R} = \text{C}_6\text{H}_5$, $\text{E} = \text{O}$ (8)). To a sample of the monophosphorus hydrazide (1-4) (1 mmol) in CH_2Cl_2 (25 mL) was added dropwise with stirring at 25°C a solution of $\text{PdCl}_2(\text{PhCN})_2$ (1 mmol) also in CH_2Cl_2 (25 mL). An orange-colored precipitate slowly appeared. The mixture was stirred for 2 h before the precipitate was filtered off and washed first with hexane (3×10 mL) and then with diethyl ether (3×10 mL). The micro-crystalline solid compounds 5-8 were then recrystallized from boiling acetonitrile.

(CH_3O) $_2\text{P}(\text{S})\text{NMeNH}_2\text{PdCl}_2$ (5): brown crystals; yield 89%; mp $<118^\circ\text{C}$ dec. ^{31}P NMR (CDCl_3): 87.5. ^1H NMR (CDCl_3): 3.87 (d, 14.1, 6H, P-OCH $_3$), 3.12 (d, $J = 9.3$ Hz, 3H, N-CH $_3$). Anal. Calcd for $\text{C}_3\text{H}_{11}\text{N}_2\text{O}_2\text{PSPdCl}_2$: C, 10.37; H, 3.19; N, 8.06; Cl, 20.41. Found: C, 10.35; H, 3.16; N, 8.05; Cl, 20.40.

($\text{C}_2\text{H}_5\text{O}$) $_2\text{P}(\text{S})\text{NMeNH}_2\text{PdCl}_2$ (6): brown powder; yield 90%; mp; $<100^\circ\text{C}$ dec. ^{31}P NMR (CDCl_3): 83.5. ^1H NMR (CDCl_3): 1.29 (t, 6H, P-OCH $_2\text{CH}_3$); 3.24 (d, $J = 9.4$ Hz, 3H, N-CH $_3$); 4.41 (m, 4H, P-OCH $_2\text{CH}_3$). Anal. Calcd for $\text{C}_5\text{H}_{15}\text{N}_2\text{O}_2\text{PSPdCl}_2$: C, 15.99; H, 4.03; N, 7.46; Cl, 18.88. Found: C, 15.97; H, 4.01; N, 7.45; Cl, 18.87.

($\text{C}_6\text{H}_5\text{O}$) $_2\text{P}(\text{O})\text{NMeNH}_2\text{PdCl}_2$ (7): brown powder; yield 85%; mp $<138^\circ\text{C}$ dec. ^{31}P NMR (CDCl_3): -4.01. ^1H NMR (CDCl_3): 2.7 (d, $J = 12.6$ Hz, 3H, N-CH $_3$); 7.1-7.6 (m, 10H, -OPh). Anal. Calcd for $\text{C}_{13}\text{H}_{15}\text{N}_2\text{O}_3\text{PPdCl}_2$: C, 34.27; H, 3.32; N, 6.15; Cl, 15.56. Found: C, 34.25; H, 3.30; N, 6.13; Cl, 15.55.

(C_6H_5) $_2\text{P}(\text{O})\text{NMeNH}_2\text{PdCl}_2$ (8): brown powder; yield 87%; mp $<141^\circ\text{C}$ dec. ^{31}P NMR (CDCl_3): 25.91. ^1H NMR (CDCl_3): 2.56 (d, $J = 11.1$ Hz, 3H, N-CH $_3$); 7.4-7.8 (m, 10H, -Ph). Anal. Calcd for $\text{C}_{13}\text{H}_{15}\text{N}_2\text{POPdCl}_2$: C, 36.86; H, 3.57; N, 6.61; Cl, 16.74. Found: C, 36.85; H, 3.56; N, 6.57; Cl, 16.73.

X-ray Data Collection and Processing

Brown colored cubic-shaped crystals of (CH_3O) $_2\text{P}(\text{S})\text{NMeNH}_2\text{PdCl}_2$ (5) were isolated from slow evaporation of mixture of dichloromethane/acetonitrile solutions at -4°C . All X-ray data were collected on an Enraf-Nonius CAD-4 diffractometer with $\text{MoK}\alpha$ radiation and a graphite monochromator at $22 \pm 1^\circ\text{C}$. Crystal data and details of data collection of compound 5 are given in Table 1. Positional parameters are summarized in Table 2. Selected bond distances and angles are listed in Table 3. The unit cell dimensions were obtained from a least-squares fit to setting angles of 25 reflections. The crystals of compound 5 exhibited no significant decay under X-ray irradiation.

The structure was solved by Patterson and Fourier methods and refined by full matrix least square methods, which minimized $\sum w(|F_o| - |F_c|)^2$ where $w^{-1} = (\sigma^2(\text{counting}) + (0.008(F_o)^2)/4F_o^2)$. Atomic scattering factors which included anomalous scattering contributions were from ref 7. There is some disorder of atoms O(2) and C(2) which is reflected in the positional parameters listed in Table 2. All of the hydrogen atoms were introduced in the last step of the refinement procedure in calculated positions. The final cycle of the least-squares refinement gave an agreement factor R of 0.035 for 5, and the highest peak in the last Fourier difference synthesis, located close to the metal atom, was 0.73 e/Å 3 . The programs used for crystallographic computations are reported in ref 8. Listings of full experimental details, coordinates, temperature factors, and anisotropic temperature factors are deposited as supplementary material.

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Table 2. Positional Parameters and Their Estimated Standard Deviations for (MeO)₂P(S)NMeNH₂·PdCl₂ (5)

	x	y	z	B _{iso} , ^a Å ²
Pd	0.341066(18)	0.35403(4)	0.02880(4)	3.26(3)
Cl(1)	0.25595(7)	0.44228(16)	-0.08882(19)	4.73(7)
Cl(2)	0.37409(8)	0.38693(19)	-0.17939(18)	5.28(9)
S	0.42499(7)	0.27049(19)	0.15224(20)	4.85(8)
P	0.40370(8)	0.20049(17)	0.32886(21)	4.42(8)
N(1)	0.34465(21)	0.2573(5)	0.3375(6)	4.02(22)
N(2)	0.31049(22)	0.3242(5)	0.2114(6)	3.53(22)
C(3)	0.3178(3)	0.2194(8)	0.4539(8)	5.0(3)
O(1)	0.44632(22)	0.2240(7)	0.4827(6)	6.6(3)
C(1)	0.4613(4)	0.3522(11)	0.5349(10)	7.6(6)
O(2)	0.3939(4)	0.0459(8)	0.3162(12)	8.3(5)
O(2')	0.4214(7)	0.0631(19)	0.3931(19)	2.2(3)
C(2)	0.4343(7)	-0.0440(16)	0.3147(17)	8.9(4)
C(2')	0.3905(11)	-0.041(3)	0.282(3)	5.0(5)
H(N2A)	0.304(3)	0.416(7)	0.231(7)	4.7
H(N2B)	0.277(3)	0.288(7)	0.178(7)	4.7
H(1A)	0.499	0.352	0.626	8.1
H(1B)	0.430	0.395	0.581	8.1
H(1C)	0.466	0.410	0.441	8.1
H(2A)	0.452	-0.028	0.219	9.7
H(2B)	0.468	-0.039	0.418	9.7
H(2C)	0.418	-0.143	0.306	9.7
H(3A)	0.291	0.136	0.414	5.7
H(3B)	0.292	0.298	0.472	5.7
H(3C)	0.350	0.197	0.553	5.7

^a B_{iso} is the mean of the principal axes of the thermal ellipsoid.**Table 3.** Selected Bond Length (Å) and Bond Angle (deg) Data for (MeO)₂P(S)NMeNH₂·PdCl₂ (5)

Bond Lengths			
Pd-Cl(1)	2.3139(18)	P-O(1)	1.556(6)
Pd-Cl(2)	2.2897(17)	P-O(2)	1.608(8)
Pd-S	2.2847(19)	P-O(2')	1.551(19)
Pd-N(2)	2.033(5)	P-O(2'')	1.427(7)
S-P	1.9654(24)	N(1)-C(3)	1.452(8)
P-N(1)	1.610(5)		
Angles			
Cl(1)-Pd-Cl(2)	92.21(7)	Cl(2)-Pd-N(2)	179.06(16)
Cl(1)-Pd-S	178.06(7)	S-Pd-N(2)	91.54(16)
Cl(1)-Pd-N(2)	87.01(16)	Pd-S-P	97.92(9)
Cl(2)-Pd-S	89.25(7)	S-P-N(1)	110.64(20)

Results and Discussion

We and others have reported that the reactions of dihalophosphorus chalcogenides RP(E)Cl₂ with methylhydrazine result in the formation of phosphorus bis(hydrazides) (RP(S)(NMeNH₂)₂).^{5,9,10} However, it was of interest to investigate the reactions of monohalophosphorus(V) precursors with methylhydrazine to explore the possibility of producing hydrazine derivatives with a single main group center on their backbone (e.g., RNMe-NH₂; R = P(V) functionality). For example, the alkoxy-, aryloxy-, and aryl-substituted phosphorus monochlorides (R₂P(E)Cl; R = OCH₃, E = S; R = OC₂H₅, E = S; R = OC₆H₅, E = O; R = C₆H₅, E = O) reacted with methylhydrazine to produce a new class of phosphorus-substituted hydrazine compounds R₂P(E)NMeNH₂: 1-methylphosphorohydrazidothioic acid, *O,O*-dimethyl ester (1); 1-methylphosphorohydrazidothioic acid, *O,O*-diethyl ester (2); 1-methylphosphorohydrazidic acid, diphenyl ester (3); diphenylphosphinic 1-methylhydrazide (4) (Scheme 2). It is imperative that the phosphorus (V) chlorides are mixed with methylhydrazine in dilute halocarbon solutions (e.g., CHCl₃ or CH₂Cl₂) at 0 °C to obtain the monophosphorus hydrazides 1-4 in good yields and to avoid side reactions which produce various other phosphorus hydrazides through the reactions at both nitrogens of methylhydrazine.

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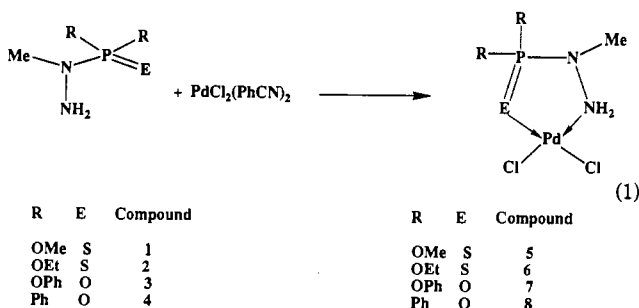
Table 4. ¹H^a and ³¹P^b NMR Spectroscopic Data^c for Monophosphorus Hydrazides (1-4) and Their Pd(II) Complexes (5-8)

compounds	¹ H NMR δ(¹ H) (³ J _{PH} , Hz)		³¹ P NMR δ(³¹ P)
	P-N-CH ₃ region	P-R region	
(OCH ₃) ₂ P(S)(NMeNH ₂) (1)	2.94 (10.8)	3.72 (13.5)	81.5
(OC ₂ H ₅) ₂ P(S)(NMeNH ₂) (2)	2.78 (8.1)	1.18, 3.97	79.55
(OPh) ₂ P(O)(NMeNH ₂) (3)	2.87 (7.8)	7.1-7.4	0.29
(Ph) ₂ P(O)(NMeNH ₂) (4)	2.62 (8.7)	7.5-7.9	29.52
(OCH ₃) ₂ P(S)(NMeNH ₂)·PdCl ₂ (5)	3.12 (9.3)	3.87 (14.1)	87.5
(OC ₂ H ₅) ₂ P(S)(NMeNH ₂)·PdCl ₂ (6)	3.24 (9.4)	1.29, 4.41	83.5
(OPh) ₂ P(O)(NMeNH ₂)·PdCl ₂ (7)	2.7 (12.6)	7.1-7.6	-4.01
(Ph) ₂ P(O)(NMeNH ₂)·PdCl ₂ (8)	2.56 (11.1)	7.4-7.8	25.91

^a Spectra in CDCl₃; ppm vs SiMe₄. ^b Spectra in CDCl₃; ppm vs 85% H₃PO₄. ^c Values quoted are those determined at normal probe temperatures.

The chemical constitutions of all the new phosphorus hydrazides 1-4 were established by C, H, and N analyses and ³¹P and ¹H spectroscopy. In the ¹H NMR spectra, the -NCH₃ signals of 1-4 appeared as clear, sharp doublets with ³J_{HP} = 7-13 Hz (Table 4). The ³¹P NMR spectra of 1-4 consisted of single sharp resonances indicative of singular chemical species. The ³¹P chemical shift ranges for 1 and 2 at 81.5 and 79.55 ppm and 3, and 4 at 0.29 and 29.52 ppm are normal for compounds containing P^v(S) and P^v(O) phosphorus centers, respectively. The hydrazine derivatives that contain aliphatic substituents (e.g., R¹R²N-NH₂; R¹ and R² = aliphatic substituents) generally show instability toward air and water. However, the P(V)-functionalized hydrazides 1-4 are kinetically inert and did not show hydrolytic instability and can be readily handled in the open atmosphere. Therefore, the reactions outlined in Scheme 2 provide a novel synthetic strategy to stabilize hydrazine backbones for subsequent use in main group and transition metal chemistry.

Reactions of Phosphorus Hydrazides 1-4 with PdCl₂(PhCN)₂. The phosphorus hydrazides 1-4 reacted smoothly with PdCl₂(PhCN)₂ in CH₂Cl₂ at 25 °C to give the new cyclopalladaphosphorohydrazides ((R)₂P(E)NCH₃NH₂·PdCl₂ (R = OCH₃, E = S (5); R = OC₂H₅, E = S (6); R = OC₆H₅, E = O (7); R = C₆H₅, E = O (8)) in good yields (eq 1).



All new metallacyclic compounds 5-8 are brown microcrystalline, air-stable solids. They are sparingly soluble in halocarbon and aromatic solvents. However, they are highly soluble in ethyl and methyl alcohols. They are also soluble in mixtures of 1:1 alcohol and water. The analytical (C, H, N, and Cl) data of the new Pd(II) metallacyclic compounds 5-8 clearly showed the complexes to have one ligand unit per metal center. The chemical compositions of all the complexes were further established by IR and ¹H and ³¹P NMR spectroscopy. A significant lowering of the wave numbers for ν(NH₂) for 5-8 by about 100-110 cm⁻¹ compared to that for the free ligands 1-4 was observed. The

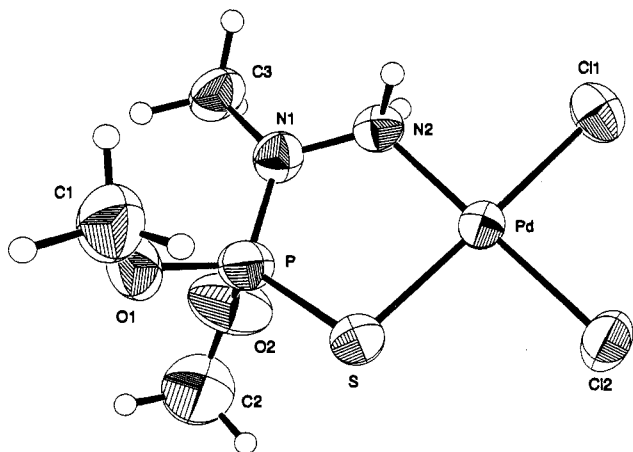


Figure 1. ORTEP drawing of the molecular structure of $(\text{OMe})_2\text{P}(\text{S})\text{-NMeNH}_2\cdot\text{PdCl}_2$ (**5**) with 50% thermal ellipsoids.

$-\text{NMe}$ signals in **5–8**, which resonated as doublets in the ^1H NMR spectra, showed a modest shift of $\sim 0.2\text{--}0.4$ ppm compared to the corresponding values in the uncomplexed ligands **1–4** (Table 4).

The ^{31}P NMR spectra of **5–8** consisted of a single sharp resonance indicating the presence of pure products. There was only a modest shift of the ^{31}P chemical shifts (by 3–5 ppm) on going from the free ligands **1–4** to the metal complexes (Table 4).

The reactions outlined in eq 1 represent a new mode of coordination of functionalized main group hydrazides with Pd(II). Therefore, an X-ray structural analysis of a Pd(II) representative **5** was undertaken with a view to understanding the bonding features of this class of metallacyclic compounds. The ORTEP plot is shown in Figure 1, and the selected bonding parameters are described in Table 3. The structure of **5** comprises a five-membered metallacyclic formulation with the Pd(II) bonded in a *cis* disposition with the hydrazido $-\text{NH}_2$ and the phosphorus chalcogenide $\text{P}=\text{S}$ groups. The square planar geometry in **5** is further characterized by a slight elongation of the Pd–Cl(1) bond (2.31 Å) as compared to the Pd–Cl(2) bond (2.28 Å), presumably a consequence of the trans influence of the $\text{P}=\text{S}$ unit. The Pd–S (2.28 Å) and the Pd–N(2) (2.03 Å) bonds are in the normal range.^{11,12}

The Pd(II) complexes of various phosphorus chalcogenides have been reported to exist in the PdX_2L_2 form ($\text{X} = \text{Cl}, \text{Br}; \text{L} = \text{Ph}_3\text{P}(\text{S}), \text{Ph}_3\text{P}(\text{Se})$).¹³ However, all these complexes are highly insoluble and show extreme hydrolytic instability. In sharp contrast, the high kinetic stability of **5–8** can be rationalized in terms of the neutralization of the electronic charge of the metal center by the basic hydrazido nitrogens.

Conclusions

The reactions of $\text{R}_2\text{P}(\text{E})\text{Cl}$ ($\text{E} = \text{O}, \text{S}$) with methylhydrazine occur exclusively at the HNMe center of MeNHNH_2 to give the new P(V)-functionalized hydrazides: $\text{R}_2\text{P}(\text{E})\text{NMeNH}_2$ ($\text{E} = \text{O}, \text{S}$) as outlined in Scheme 2. The introduction of a P(V) center on the methyl hydrazine backbone (e.g., **1–4**) induces remarkable hydrolytic stability to the hydrazine skeleton as compared to the unfunctionalized free methylhydrazine HNMeNH_2 . Therefore, the new phosphorus hydrazides **1–4** may be regarded as the “hybrids” of methylhydrazine. The substitution reactions of methylhydrazine with the phosphorus(V) halides as outlined in Scheme 2 introduce new coordination sites such as P(O) or P(S) to be used for the heteroatomic chelation (e.g., SN coordination in **5** and **6** and ON coordination in **7** and **8**) with the transition metals (eq 1).

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Supplementary Material Available: Tables giving an extended listing of bond lengths and angles, full crystallographic and experimental data, anisotropic thermal parameters, and hydrogen atom coordinates (5 pages). Ordering information is given on any current masthead page.

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