Transition Metal Chemistry of Main Group Hydrazides. 1. Synthesis and Characterization of Cyclometallaphosphohydrazides of Cobalt(I), Copper(I), and Palladium(II). X-ray Structures of Cobalt(I) and Palladium(II) Representatives

Kattesh V. Katti,[*,†] Prahlad R. Singh,[‡] and Charles L. Barnes[‡]

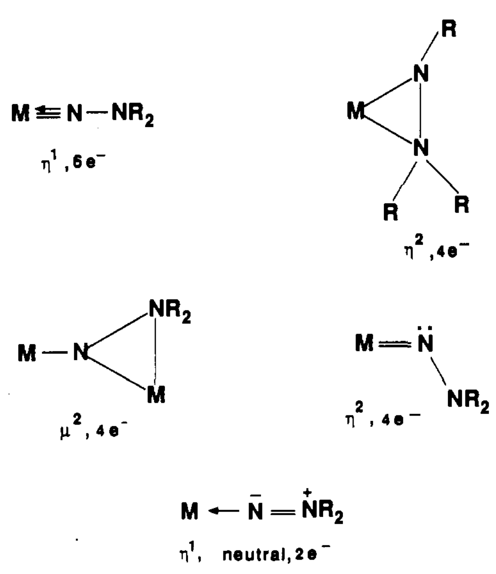
Departments of Radiology and Chemistry, 409 Lewis Hall, University of Missouri, Columbia, Missouri 65211

Received January 13, 1992

The reactions of the phosphohydrazide $PhP(S)(NMeNH_2)_2$ (**1**) with the perchlorates of Co(II) and Cu(II) led to the formation of spirocyclic cyclometallaphosphohydrazides containing Co(I) (**2**) and Cu(I) (**3**) metal centers. Compound **1** in its reaction with $PdCl_2(PhCN)_2$ produced the Pd(II) metallacycle **4** wherein coordination with the metal center occurs through P=S and one of the hydrazine $-NH_2$ units. Phosphohydrazide **1** undergoes Schiff base reactions with aromatic- and aliphatic-substituted aldehydes such as salicylaldehyde and piperazinecarboxaldehyde to give new phosphohydrazide ligands **5** and **6**, respectively, in high yields. The Pd(II) metallacycles **7** and **8** obtained from the reactions of **5** and **6** respectively showed similar ligating characteristics as in **4**. The structural elucidation of all the new ligands and the cyclometallaphosphohydrazides has been done by analytical and complete NMR (^1H, ^{31}P) and IR spectroscopic data. The structures of **2** and **7** were further confirmed by X-ray diffraction study. Crystal data for **2**: monoclinic space group $P2_1/c$, $a = 12.362$ (4) Å, $b = 11.013$ (9) Å, $c = 10.842$ (3) Å, $\beta = 100.08$ (9)°, $Z = 4$. Crystal data for **7**: triclinic space group $P\bar{1}$, $a = 9.491$ (3) Å, $b = 11.480$ (20) Å, $c = 12.896$ (4) Å, $\beta = 88.170$ (15)°, $Z = 2$. The structures were solved by direct methods and were refined to $R = 0.030$ and 0.028 for **2** and **7** respectively.

Introduction

Hydrazine ligands continue to be an important class of nitrogen-based ligands in the chemistry of early and late transition metals.[1–6] The involvement of transition metal hydrazides in the chemical and biological nitrogen fixation phenomena may be regarded as a premier example of the useful reactivity of this class of compounds.[7,8] The different bonding modes, as shown here,



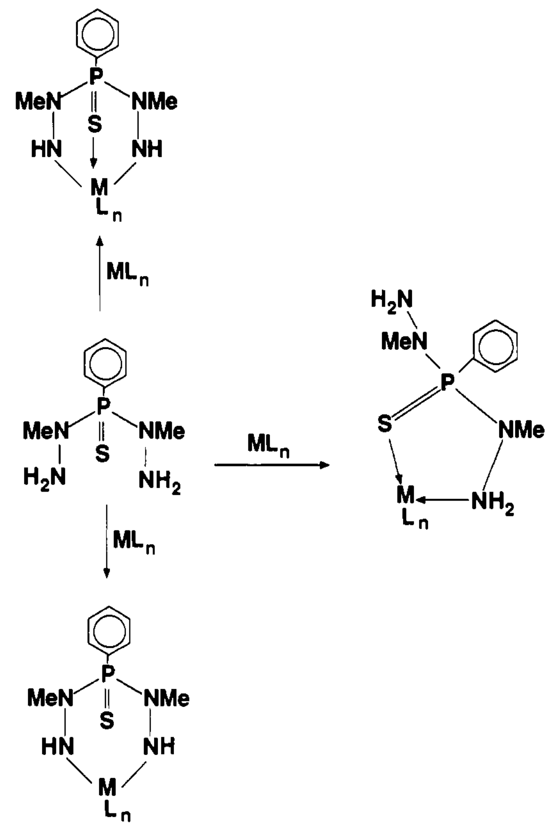
clearly indicate the versatility of hydrazine ligands in transition metal chemistry.[4,5] The incorporation of hydrazine units in chelating frameworks may aid in the understanding of new reactivity trends of such ligands with transition metals. The high reactivity of the parent hydrazine (N_2H_4) should allow the incorporation of additional donor sites such as SH, OH, or even an additional hydrazine fragment (i.e. $RN-NR_2$) on the hydrazine backbone to promote chelation and hence provide extra stability to the metal centers bound to the hydrazine ligands. This approach of using hydrazine units in chelating frameworks with transition metals 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. For example, a chelating hydrazine skeleton ligand **1** may interact with a transition metal in three different tangible ways (Scheme I). In this paper, through the synthesis of novel Co(I), Cu(I), and Pd(II) complexes of **1** and related ligands, we demonstrate the versatility and the general applicability of chelating hydrazine

* Author to whom correspondence should be addressed.
† Department of Radiology.
‡ Department of Chemistry.

(1) (a) Pickett, C. J.; Talarmin, J. *Nature (London)* **1985**, *317*, 652. (b) Pickett, C. J.; Ryder, K. S.; Tolarmin, J. *J. Chem. Soc., Dalton Trans.* **1986**, 1453.
(2) Chatt, J.; Dillworth, J. R.; Richards, R. L. *Chem. Rev.* **1978**, *78*, 589.
(3) (a) Abrams, M. J.; Larsen, S. K.; Zubieta, J. *Inorg. Chem.* **1991**, *30*, 2031. (b) Nicholson, T.; Zubieta, J. *Inorg. Chem.* **1987**, *26*, 2094. (c) Nicholson, T.; Lombardi, P.; Zubieta, J. *Polyhedron* **1987**, *7*, 1577. (d) Nicholson, T.; Zubieta, J. *Inorg. Chim. Acta* **1987**, *134*, 191. (e) Nicholson, T.; Shaikh, N.; Zubieta, J. *Inorg. Chim. Acta* **1985**, *99*, L45.
(4) (a) Archer, C. M.; Dilworth, J. R.; Jobanputra, P.; Thompson, R. M.; McPartlin, M.; Povey, D. C.; Smith, G. W.; Kelly, J. D. *Polyhedron* **1990**, *9*, 1497. (b) Dilworth, J. R.; Harrison, S. A.; Walton, D. R. M.; Schweda, E. *Inorg. Chem.* **1985**, *24*, 2594. (c) Dilworth, J. R.; Latham, I. A.; Leigh, G. J.; Huttner, G.; Jibril, I. *J. Chem. Soc., Chem. Commun.* **1983**, 1368. (d) Johnson, B. F. G.; Haymore, B. L.; Dilworth, J. R. In *Comprehensive Coordination Chemistry*; Wilkinson, R., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, England, 1987; Vol. 2, pp 99–159 and references therein.
(5) (a) Shapiro, P. J.; Henling, L. M.; Marsh, R. E.; Bercaw, J. E. *Inorg. Chem.* **1990**, *29*, 4560. (b) Nugant, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123–175. (c) Murray, R. C.; Schrock, R.-P. *J. Am. Chem. Soc.* **1985**, *107*, 4557. (d) Schrock, R. R.; Liu, A. H.; O'Regan, M. B.; Finch, W. C.; Payak, J. F. *Inorg. Chem.* **1988**, *27*, 3574 and references therein.
(6) (a) Latham, J. A.; Leigh, G. J. *J. Chem. Soc., Dalton Trans.* **1986**, 399. (b) Clark, C. C. *Hydrazine*; Mathieson Chemical Corp.: MD, 1953; Chapter 1.
(7) Thorneley, R. N. F.; Lowe, D. J. In *Molybdenum Enzymes*; Spiro, T. G., Ed.; John Wiley and Sons: New York, 1985; Chapter 5, p 221.
(8) Henderson, R. A.; Leigh, G. J.; Pickett, C. J. *Adv. Inorg. Radiochem.* **1983**, *27*, 197.

0020-1669/92/1331-4588$03.00/0

Scheme I



ligands of the type **1** to develop new transition metal chemistries of different metals.

Experimental Section

Unless otherwise stated, all reactions were carried out under anaerobic and anhydrous conditions using prepurified N_2 and conventional Schlenk techniques. Reagents such as $Co(ClO_4)_2{\cdot}6H_2O$, $Cu(ClO_4)_2{\cdot}6H_2O$, $P(S)PhCl_2$ and $PdCl_2$ were purchased from Aldrich Chemical Co. and were used without further purification. Phosphorousbis(hydrazide)sulfide (BHPS) **1** was prepared by the reaction of $PhP(S)Cl_2$ with methyl hydrazine.[9,10]

Nuclear magnetic resonance spectra were recorded on a Bruker WH-500 spectrometer. The ^1H NMR chemical shifts are reported in parts per million (ppm) downfield from external standard $SiMe_4$. The ^{31}P NMR spectra were recorded with 85% H_3PO_4 as an external standard, and positive shifts lie downfield of the standard.

Synthesis of Complex 2. To a solution of **1** (4.7 g, 20.25 mmol) in absolute ethanol (100 mL) was added dropwise with stirring at 0 °C a solution of $Co(ClO_4)_2{\cdot}6H_2O$ (2.47 g, 6.74 mmol) also in absolute ethanol (50 mL). Upon completion of addition (30 min), a pink solid precipitated out. The mixture was stirred at 25 °C for 6 h before the solid precipitate was filtered and dried in air to obtain **2** as a shiny light pink crystalline solid. Recrystallization from hot acetonitrile produced transparent pink flakes of analytically pure **2**, which was recrystallized from boiling absolute ethanol (yield 3.93 g; 94% based on $Co(ClO_4)_2{\cdot}6H_2O$); mp 180 °C dec. Anal. Calcd for $C_{16}H_{30}N_8ClO_4P_2S_2Co$: C, 31.04; H, 4.85; N, 18.11; Cl, 5.73. Found: C, 31.02; H, 4.87; N, 18.10; Cl, 5.76.

Synthesis of Complex 3. To a solution of **1** (4.53 g, 19.70 mmol) in THF (150 mL) was added dropwise (30 min) with stirring at 0 °C a solution of $Cu(ClO_4)_2{\cdot}6H_2O$ (1.82 g, 4.92 mmol) in absolute ethanol (50 mL). The mixture on stirring at 25 °C for 8 h turned greenish with suspensions of similar colored solid precipitate. The solvents were removed under vacuo and the crystalline residue was washed successively (4 × 25 mL) with THF to remove the unreacted excess of **1**. The leftover green solid was boiled in absolute ethanol to obtain green colored cubic crystals of **3** and was recrystallized from boiling absolute ethanol (yield 2.80 g, 91% based on $Cu(ClO_4)_2{\cdot}6H_2O$); mp 194 °C. Anal. Calcd for $C_{16}H_{30}N_8ClO_4P_2S_2Cu$: C, 30.81; H, 4.81; N, 17.97; Cl, 5.69. Found: C, 30.84; H, 4.83; N, 17.96; Cl, 5.71.

Synthesis of Complex 4. A solution of $PdCl_2(PhCN)_2$ (3.53 g, 9.22 mmol) in CH_2Cl_2 (100 mL) was added dropwise (15 min) at 25 °C to a solution of **1** (2.12 g, 9.22 mmol) also in CH_2Cl_2 (100 mL). The dark orange-colored mixture on stirring for 4 h turned yellow, and the solvent was removed in vacuo to obtain a brown microcrystalline solid which upon washing with THF (2 × 10 mL) gave analytically pure **4**, which was recrystallized from boiling acetonitrile (yield 3.42 g, 91%); mp 210 °C dec. Anal. Calcd for $C_8H_{15}N_4Cl_2PSPd$: C, 23.56; H, 3.68; N, 13.74; Cl, 17.40. Found: C, 23.54; H, 3.70; N, 13.71; Cl, 17.51.

Synthesis of Compound 5. To a solution of **1** (3.50 g, 15.26 mmol) in absolute ethanol (100 mL) was added dropwise (15 min) at 25 °C with stirring a solution of salicylaldehyde (3.81 g, 31.28 mmol) in absolute ethanol (100 mL). The mixture was stirred under reflux for 12 h before the solvent was removed under vacuo to obtain a white crystalline solid of **5**, which was recrystallized from boiling acetonitrile (yield 6.40 g, 96%); mp 89 °C. Anal. Calcd for $C_{22}H_{23}N_4O_2PS$: C, 60.22; H, 5.25; N, 12.78. Found: C, 60.21; H, 5.21; N, 12.74.

Compound 6 was synthesized by the reaction of **1** with piperazinecarboxaldehyde under identical reaction conditions as described above for **5**. Recrystallization from $CH_3CN/CHCl_3$ (3:1) (yield 88%); mp 109 °C. Anal. Calcd for $C_{18}H_{31}N_8PS$: C, 51.11; H, 7.34; N, 26.52. Found: C, 51.14; H, 7.37; N, 26.50.

Synthesis of Complex 7. To a solution of **5** (2.95 g, 6.76 mmol) in THF (100 mL) was added with stirring at 25 °C a solution of $PdCl_2(PhCN)_2$ (2.58 g, 6.73 mmol) also in THF (50 mL). The reaction mixture was heated under reflux for 2 h before the solvent was removed under vacuo to obtain a brown microcrystalline solid of **7**. The crude **7** was washed with chilled CH_2Cl_2 (2 × 10 mL) to remove the residual benzonitrile before it was recrystallized from acetonitrile (yield 3.60 g, 92%); mp 151 °C dec. Anal. Calcd for $C_{22}H_{22}N_4ClO_2PSPd$: C, 45.64; H, 3.83; N, 9.67; Cl, 6.12. Found: C, 45.57; H, 3.84; N, 9.70; Cl, 6.10.

Synthesis of Complex 8. To a suspension of **6** (2.75 g, 6.51 mmol) in dichloromethane (50 mL) was added with stirring at 25 °C a solution of $PdCl_2(PhCN)_2$ (2.49 g, 6.51 mmol), also in dichloromethane (50 mL). The mixture was stirred for 6 h before the solvent was removed in vacuo to obtain **8** as an orange-colored microcrystalline solid. Recrystallization from boiling CH_3CN gave analytically pure **8** (yield 3.25 g, 83%); mp 163 °C dec. Anal. Calcd for $C_{18}H_{31}N_8Cl_2PSPd$: C, 36.02; H, 5.17; N, 18.67; Cl, 11.82. Found: C, 36.11; H, 5.15; N, 18.63; Cl, 11.84.

Table I. Crystallographic Data for **2** and **7**

	2	7
formula	$^1/_2[C_{16}H_{30}N_8P_2S_2Co]ClO_4$	$C_{22}H_{22}N_4O_2PSClPd{\cdot}CH_3CN$
fw	388.67	620.39
cryst syst	monoclinic	triclinic
space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
a, Å	12.362 (4)	9.491 (3)
b, Å	11.0131 (9)	11.4840 (20)
c, Å	10.842 (3)	12.896 (4)
β, deg	100.048 (9)	88.170 (15)
V, Å^3	1453.4 (6)	1335.3 (6)
Z	4	2
T, °C	22 (1)	22 (1)
d_{calcd}, g cm^{-3}	1.776	1.543
μ, cm^{-1}	16.3	10.5
R^a	0.030	0.028
R_w^b	0.042	0.036

[a] $R = \sum[|F_o| - |F_c|]/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum|F_o|^2]^{1/2}$, where $w = 1/[\sigma^2|F_o| + 0.0008\,(F_o)^2]$.

X-ray Data Collection and Processing

Transparent pink cubic-shaped crystals of **2** and orange-colored blocklike crystals of **7** were isolated from slow evaporations of absolute ethanol and acetonitrile solutions, respectively. All X-ray data were collected on an Enraf-Nonius CaD4 diffractometer with Mo Kα radiation and a graphite monochromator at 22 (1) °C. Crystal data and details of data collection are given in Table I. The unit cell dimensions were obtained from a least squares fit to setting angles of 25 reflections. The crystals of **2** and **7** exhibited no significant decay under X-ray irradiation.

The structures were solved by Patterson and Fourier methods and refined by full matrix least square methods, which minimized $\sum w(|F_o| - |F_c|)^2$ where $w^{-1} = (\sigma^2(\text{counting}) + (0.008(F_o^2)^2/4F_o^2$. Atomic scattering factors which included anomalous scattering contributions were from ref

(9) Katti, K. V.; Singh, P. R.; Volkert, W. A.; Ketring, A. R.; Katti, K. K. *Int. J. Appl. Radiat. Isot.*, in press.
(10) Majoral, J. P.; Kramer, R.; Navech, J.; Mathis, F. *Tetrahedron* **1976**, *32*, 2633.

Table II. Positional Parameters and Their Estimated Standard Deviations for **2**

	x	y	z	B_{eq},[a] Å^2
Co1	0	0	0	2.36 (3)
P	−0.18493 (6)	0.08908 (8)	0.11546 (8)	2.29 (4)
S	−0.07286 (7)	0.19693 (8)	0.06414 (9)	3.05 (4)
N1	−0.12886 (22)	−0.0097 (3)	0.22577 (24)	2.58 (11)
N2	−0.0425 (3)	−0.0745 (3)	0.1766 (3)	2.95 (14)
N3	−0.24338 (22)	0.0095 (3)	−0.0075 (3)	2.97 (12)
N4	−0.1667 (3)	−0.0450 (4)	−0.0762 (3)	3.12 (15)
C1	−0.0903 (4)	0.0334 (5)	0.3537 (4)	4.06 (21)
C3	−0.3516 (3)	−0.0452 (5)	−0.0252 (5)	4.15 (20)
C11	−0.2954 (3)	0.1603 (3)	0.1745 (3)	2.70 (14)
C12	−0.3517 (3)	0.1013 (4)	0.2562 (4)	3.43 (17)
C13	−0.4402 (3)	0.1588 (5)	0.2943 (4)	4.11 (20)
C14	−0.4708 (4)	0.2724 (5)	0.2507 (5)	5.12 (23)
C15	−0.4154 (4)	0.3301 (5)	0.1702 (6)	5.7 (3)
C16	−0.3267 (3)	0.2765 (4)	0.1327 (4)	4.06 (19)
Cl	0.23917 (7)	0.36736 (9)	0.90717 (8)	3.32 (4)
O1	0.18509 (22)	0.47601 (25)	0.8570 (3)	4.36 (13)
O2	0.2724 (4)	0.2996 (4)	0.8094 (3)	8.38 (22)
O3	0.1654 (3)	0.2963 (3)	0.9628 (4)	6.66 (18)
O4	0.3312 (3)	0.3965 (4)	0.9971 (4)	8.33 (21)

[a] B_{eq} is the mean of the principal axes of the thermal ellipsoid.

11. All the hydrogen atoms in **2** were located and refined with fixed isotropic thermal parameters. The final cycle of the least-squares refinement gave an agreement factor R of 0.030 for **2**, and the highest peak in the last Fourier difference synthesis, located close to the metal atom, was 0.33 e/Å^3. For **7** the hydroxy hydrogen, connected to O(2), was located and refined with fixed isotropic thermal parameters. All the remaining hydrogen atoms of **7** were introduced in the last step of the refinement procedure in calculated positions. The final agreement factor (R) for **7** = 0.028 with the highest residual peak at 0.30 e/Å^3. Atomic positional parameters are listed in Table II for **2** and in Table III for **7**. The programs used for crystallographic computations are reported in ref 12. Listings of full experimental details, coordinates, temperature factors, and anisotropic temperature factors, are deposited as supplementary material.

Results and Discussion

I. Reactions of BHPS (1) with Cobalt and Copper Perchlorates. The interaction of cobalt perchlorate hexahydrate $Co(ClO_4)_2 \cdot 6H_2O$ with phosphorousbis(hydrazide)sulfide (BHPS) **1** (Scheme II) in equivalent amounts at 25 °C in absolute ethanol produced a light pink precipitate and an orange-red supernated solution. The chemical constitution of this precipitate as indicated by the elemental analysis consisted of two units of **1** and one unit of $Co(ClO_4)$, whereas the orange-red filtrate on evaporation was found to be unreacted $Co(ClO_4)_2 \cdot 6H_2O$. The ^{31}P NMR spectrum of the reaction mixture, besides a sharp singlet which is a major peak for **2** at 86.0 ppm, showed closely spaced signals in the region 45–50 ppm. These signals may be attributed to the products originating from the redox reaction of **1** with $Co(ClO_4)_6 \cdot 6H_2O$. These impurities were separated by washing crude **2** from chilled ethanol or by recrystallization of the product from hot ethanol. The yield of this light brown precipitate did not increase beyond 15–20% when equivalent amounts of BHPS (**1**) and $Co(ClO_4)_2 \cdot 6H_2O$ were used. This observation in conjunction with the analytical data for this new compound indicated the spirocyclic structure **2** for the cobalt(I) complex. Repeated experiments using 3–4 equiv of BHPS (**1**) for every equivalent of $Co(ClO_4)_2 \cdot 6H_2O$ produced **2** almost quantitatively. With such a stoichiometry some unreacted **1** was also recovered; however, the excess of **1** is conceivably required to reduce the Co(II) species to Co(I) as formulated in **2**. The new spirocyclic cyclometallaphosphohydrazide **2** is air stable and dissolves readily in absolute ethanol on warming.

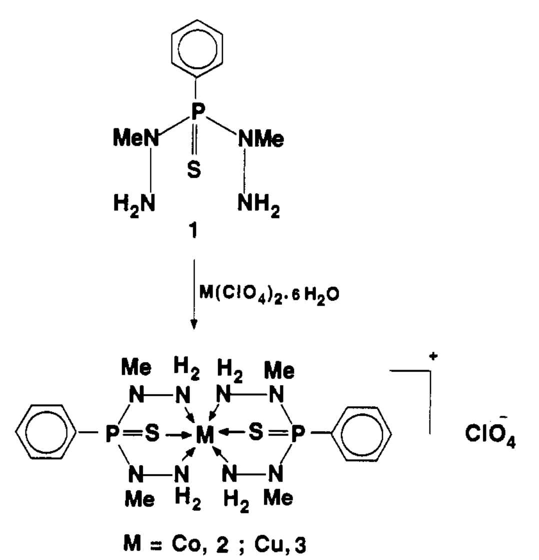
(11) *International Tables for Crystallography*: Kynoch: Birmingham, England, 1974; Vol. IV.
(12) Gabe, E. J.; LePage, Y.; Charland, J.-P.; Lee, F. E. *J. Appl. Crystallogr.* **1989**, *22*, 384–387.

Table III. Positional Parameters and Their Estimated Standard Deviations for **7**

	x	y	z	B_{eq},[a] Å^2
Pd	0.42304 (4)	0.40460 (3)	0.094927 (24)	2.739 (14)
Cl	0.22557 (11)	0.56750 (10)	0.14202 (9)	3.74 (5)
S	0.56422 (13)	0.47865 (11)	0.19680 (10)	3.94 (5)
P	0.73194 (12)	0.32485 (10)	0.20323 (8)	2.93 (5)
O1	0.2817 (3)	0.3497 (3)	0.01490 (24)	4.10 (15)
C1	0.3164 (5)	0.2569 (4)	−0.0419 (3)	3.26 (21)
C2	0.1985 (5)	0.2285 (4)	−0.0907 (3)	3.87 (22)
C3	0.2234 (6)	0.1325 (5)	−0.1515 (4)	4.50 (25)
C4	0.3663 (6)	0.0577 (5)	−0.1710 (4)	5.2 (3)
C5	0.4818 (6)	0.0801 (5)	−0.1254 (4)	4.7 (3)
C6	0.4609 (5)	0.1785 (4)	−0.0601 (3)	3.47 (21)
C7	0.5921 (5)	0.1866 (4)	−0.0129 93)	3.55 (21)
N1	0.5981 (4)	0.2673 (3)	0.0519 (3)	2.93 (16)
N2	0.7386 (4)	0.2605 (3)	0.0901 (3)	3.18 (16)
C8	0.8695 (5)	0.1659 (4)	0.0549 (4)	4.03 (22)
N3	0.8961 (4)	0.3461 (3)	0.2078 (3)	3.10 (16)
C9	0.9400 (5)	0.4218 (5)	0.1263 (3)	4.06 (23)
N4	0.9541 (3)	0.3350 (3)	0.30784 (25)	2.84 (15)
C10	1.0564 (4)	0.3826 (4)	0.3232 (3)	3.13 (20)
C11	1.1191 (4)	0.3720 (4)	0.4261 (3)	3.22 (19)
C12	1.2270 (5)	0.4304 (5)	0.4405 (4)	4.24 (23)
C13	1.2880 (5)	0.4250 (5)	0.5378 (4)	4.9 (3)
C14	1.2436 (6)	0.3644 (5)	0.6188 (4)	5.1 (3)
C15	1.1361 (6)	0.3091 (5)	0.6072 (4)	4.9 (3)
C16	1.0744 (5)	0.3126 (4)	0.5107 (3)	3.82 (22)
O2	0.9686 (4)	0.2566 (3)	0.5048 (3)	5.18 (19)
C17	0.7210 (5)	0.2181 (4)	0.3080 (3)	3.26 (20)
C18	0.8385 (5)	0.1128 (4)	0.3269 (3)	3.80 (22)
C19	0.8255 (7)	0.0264 (5)	0.4026 (4)	5.0 (3)
C20	0.6952 (9)	0.0440 (6)	0.4568 (4)	6.3 (4)
C21	0.5773 (7)	0.1475 (6)	0.4375 (5)	6.3 (3)
C22	0.5909 (6)	0.2343 (5)	0.3633 (4)	4.6 (3)
NCN	0.1401 (7)	0.9288 (7)	0.2145 (6)	10.2 (4)
CCN1	0.2143 (7)	0.8546 (7)	0.2632 (6)	7.0 (4)
CCN2	0.3120 (8)	0.7567 (1)	0.3245 (5)	7.8 (4)
HO2	0.935 (5)	0.273 (5)	0.449 (4)	4.7

[a] B_{eq} is the mean of the principal axes of the thermal ellipsoid.

Scheme II



Ethanolic solutions of **2** on cooling to 0 °C gave transparent pink cubic crystals which were used for single-crystal X-ray structural analysis. The ORTEP plot shown in Figure 1 confirms the structural formulation of **2**. Compound **2** represents the first example of a structurally characterized cobalt(I) complex with a hydrazide ligand. The crystallographic parameters of **2** appear in Table I and the selected bonding parameters are described in Table IV. The Co–N(2) and Co–N(2)a bonds are 15σ longer than Co–N(4) and Co–N(4)a and they are all in the normal range as reported for the non-hydrazine Co–NH_2 coordinate

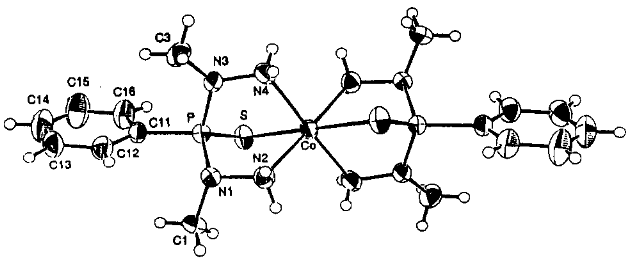


Figure 1. ORTEP drawing of the molecular structure of compound **2** with 50% thermal ellipsoids.

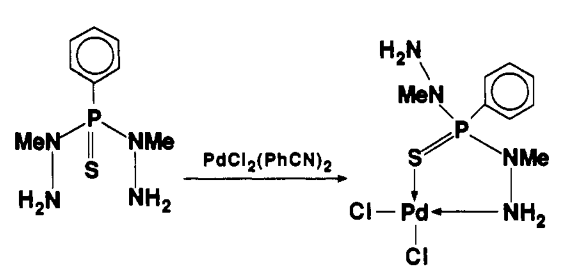
Table IV. Selected Bond Length and Bond Angle Data for **2**

	Bond Lengths (Å)		
Col–S	2.4934 (9)	P-N(1)	1.675 (3)
Col–Sa	2.4934 (9)	P-N(3)	1.653 (3)
Col-N2	2.228 (3)	N(1)-N(2)	1.460 (4)
Col-N2a	2.228 (3)	N(1)-C(1)	1.465 (5)
Col-N4	2.141 (3)	N(3)-N(4)	1.434 (4)
Col-N4a	2.141 (3)	N(3)-C(3)	1.448 (5)
P-S	1.9771 (12)		
	Bond Angles (deg)		
S–Col–Sa	180.0	Col–S–P	82.00 (4)
S–Col–N2	85.97 (9)	P–N1–N2	107.12 (20)
S–Col–N2a	94.03 (9)	P–N1–C1	119.4 (3)
S–Col–N4	86.47 (10)	N2–N1–C1	111.5 (3)
S–Col–N4a	93.53 (10)	Col–N2–N1	115.55 (20)
Sa–Col–N2	94.03 (9)	P–N3–N4	113.89 (21)
Sa–Col–N2a	85.97 (9)	P–N3–C3	126.2 (3)
Sa–Col–N4	93.53 (10)	Col–N4–N3	112.45 (21)
Sa–Col–N4a	86.47 (10)	N4–N3–C3	115.8 (3)
N2–Col–N2a	180.0	N4–Col–N4a	180.0
N2–Col–N4	83.73 (14)	S–P–N1	111.60 (11)
N2a–Col–N4	96.27 (14)	S–P–N3	108.72 (11)
N2a–Col–N4a	83.73 (14)	N1–P–N3	107.42 (15)

bonds.[13] In the crystallographic investigation of **2** all the N–H hydrogens have been located and this observation rules out any deprotonation of hydrogens and confirms the unipositive oxidation state of Co in **2**. The ^{1}H NMR spectroscopic data for **2**, discussed in a later section, corroborates the above X-ray crystallographic findings. The average N–N bond length in **2** (1.447 Å) is in the same range as those reported for some of the M–NR–NH_2[6] and M–NH–NH_2 types of complexes of different transition metals. The bonding of four terminal NH_2 groups and two sulfurs from the two units of BHPS (**1**) provide the octahedral environment around the central Co(I) unit. The six-membered PN_4Co ring system in **2** adopts a boat conformation with the phosphorus and cobalt centers deviating from the plane of the ring.

There is an extensive chemistry of cobalt in which phosphines or phosphites stabilize the unipositive oxidation state of the metal.[14] The stability of the Co(I) cation in **2** is unique and suggests that the σ-donating influence of the hydrazine nitrogens in combination with the highly nucleophilic phosphorus sulfide can be effectively used to produce complexes of cobalt and the related metals in their lower oxidation states. The interaction of the corresponding $Cu(ClO_4)_2{\cdot}6H_2O$ with an excess of BHPS (**1**) produced **3** almost quantitatively (Scheme II), and its chemical constitution was established from C, H, N, and Cl analysis. The coordination chemistry of such copper(I) compounds is of interest because of the involvement of Cu(I) species at cuproprotein active sites.[15]

II. Reactions of BHPS (1) and Related Ligands with Pd(II) Precursors. The phosphorus hydrazide **1** reacted smoothly with $PdCl_2(PhCN)_2$ to give the Pd(II) metallacyclic compound **4** in high yields (eq 1). The Pd(II) compound **4** is air stable and



1 4 (1)

dissolves readily in ethyl alcohol and is stable and sparingly soluble in water. The chemical constitution of **4** was established by C, H, N, and Cl analysis. The ^{1}H NMR spectrum clearly showed the presence of two types of -NMe groups (Table V) and indicates the presence of free and coordinated hydrazine arms.

The terminal-NH_2 units of **1** can be readily functionalized through facile Schiff base coupling reactions to produce a series of new cyclometallaphosphohydrazide compounds **5** and **6** as shown in Scheme III. The chemical compositions of all the new ligands were established by analytical and spectroscopic data (Table V). The reactions in Scheme IV illustrate the reactivity of the new ligands **5** and **6** with $PdCl_2(PhCN)_2$. The analytical data of the new Pd(II) metallacyclic compounds clearly showed the complexes to have one ligand unit per metal center. The presence of two -NMe signals (Table V) in each of the complexes **7** and **8** indicated that only one arm of the hydrazine backbone is involved in the coordination as formulated in Scheme III. The evidence for the loss of chlorine from $PdCl_2$ as formulated for **7** came from its chlorine analysis. However, the final structural proof was obtained from the X-ray structural analysis. The ORTEP plot is shown in Figure 2, and the selected bonding parameters are described in Table VI. The structure shown in Figure 2 confirms the elimination of HCl from the reaction of $PdCl_2$ with the *o*-hydroxy group in **5** to give a six-membered Pd(II) metallacycle. The square planar geometry of Pd(II) in **7** is further characterized by a five membered heterocyclic ring system involving the coordination of P=S unit and the terminal hydrazide nitrogen of **5** with the metal center. The Pd—O σ bond distance in **7** is comparable to those found in other cyclopalladated Pd(II) complexes.[16] The Pd—S and the Pd—N coordinate bonds are also in the normal range.[17,18] The presence of the coordinated and the uncoordinated functionalities such as P—N, N—N, and C=N within the same molecule **7** has allowed us to make some internally consistent comparisons of bonding features. For example, the P—N and N—N distances within the metallacyclic part of **7** are very close to the distances in the uncoordinated part of this molecule. However, the C—N bond of the Pd(II) metallacycle has suffered some elongation compared to the C=N bond in the free Schiff base coupled hydrazine arm of **7**. Assuming that the P=S bonds in the phosphohydrazides of types **1** and **5** do not change significantly with variations in the

(13) (a) Rotzinger, F. P.; Marty, W. *Inorg. Chem.* **1983**, *22*, 3593. (b) Brown, S. J.; Olmstead, M. M.; Mascharak, P. K. *Inorg. Chem.* **1989**, *28*, 3720.

(14) (a) Klein, H. F.; Konig, H.; Koppert, S.; Ellrich, K.; Riede, J. *Organometallics* **1987**, *6*, 1341. (b) Alnaji, O.; Peres, Y.; Dahan, F.; Dartiguenave, M.; Dartiguenave, Y. *Inorg. Chem.* **1986**, *25*, 1383. (c) Klein, H. F. *Z. Naturforsch.* **1985**, *40B*, 1377. (d) Socol, S. M.; Verkade, J. G. *Inorg. Chem.* **1986**, *25*, 2658.

(15) (a) Lerch, K. In *Copper Proteins*; Sigel, H., Ed.; Metal Ions in Biological Systems, 13; Marcel Dekker: New York, 1981; Chapter 5. (b) Loehr, T. M.; Sanders-Loehr, J. In *Copper Proteins and Copper Enzymes*; Lontie, R., Ed.; CRC Press: Boca Raton, FL, 1984; Vol. I, Chapter 5. (c) Solomon, E. I. in *Copper Proteins*; Spiro, T. G., Ed.; Wiley: New York, 1981; Chapter 2. (d) Préaux, G.; Gielens, C. In *Copper Proteins and Copper Enzymes*; Lontie, R., Ed.; CRC Press: Boca Raton, FL, 1984; Vol. II, Chapter 6.

(16) (a) Ghedini, M.; Morrone, S.; Munno, G. De; Crispini, A. *J. Organomet. Chem.* **1991**, *415*, 281. (b) Ghedini, M.; Pellegrino, C.; Armentano, S.; Munno, G. De; Bruno, G. *Inorg. Chim. Acta* **1986**, *122*, 193. (c) Iannelli, P.; Immirzi, A.; Caruso, U.; Roviello, A.; Sirigu, A. *Acta Crystallogr. Sect. C* **1989**, *45*, 879.

(17) (a) Yamauchi, O.; Takani, M.; Toyoda, K.; Masuda, H. *Inorg. Chem.* **1990**, *29*, 1856. (b) Boer, F. P.; Carter, V. B.; Turley, J. W. *Inorg. Chem.* **1971**, *10*, 651. (c) Katti, K. V.; Batchelor, R. J.; Einstein, F. W. B.; Cavell, R. G. *Inorg. Chem.* **1990**, *29*, 808.

(18) (a) Anillo, A.; Amico, D. B. D.; Calderazzo, F.; Nardeli, M.; Pelizzi, G.; Rocchi, L. *J. Chem. Soc., Dalton Trans.* **1991**, 2845. (b) Skapski, A. C.; Smart, M. L. *Chem. Commun.* **1970**, 658.

Table V. [1]H[a] and [31]P[b] NMR and IR[c] Spectroscopic Data

compd	[1]H NMR δ([1]H) ([3]J(P–H),Hz) in P–N–CH$_3$ region	[31]P NMR δ([31]P)	IR(cm^{-1}) ν(NH$_2$)	IR(cm^{-1}) ν(P=S)[d]
1	2.82 (11.8)	86.00	3264, 3163	696
2	2.90 (12.0)	88.50	3060	545
3			3055	547
4	3.24 (11.4); 2.75 (8.5)	87.30	3250, 3052	550
5	3.25 (9.4)	80.60		610
6	2.83 (11.6)	78.03		610
7	3.40 (10.2); 3.21 (9.4)	84.00		550
8	3.50 (9.9); 3.18 (9.1)	81.79		555

[a] All spectra in CDCl$_3$; ppm vs SiMe$_4$. [b] All spectra in CDCl$_3$; ppm vs 85% H$_3$PO$_4$. Values quoted are those determined at normal probe temperatures. [c] Spectra recorded using Nujol mulls. [d] Spectra recorded in KBr cells.

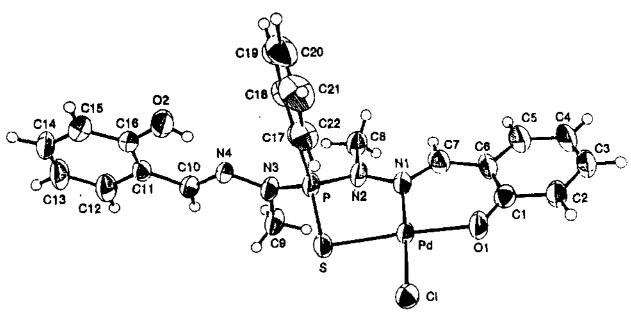
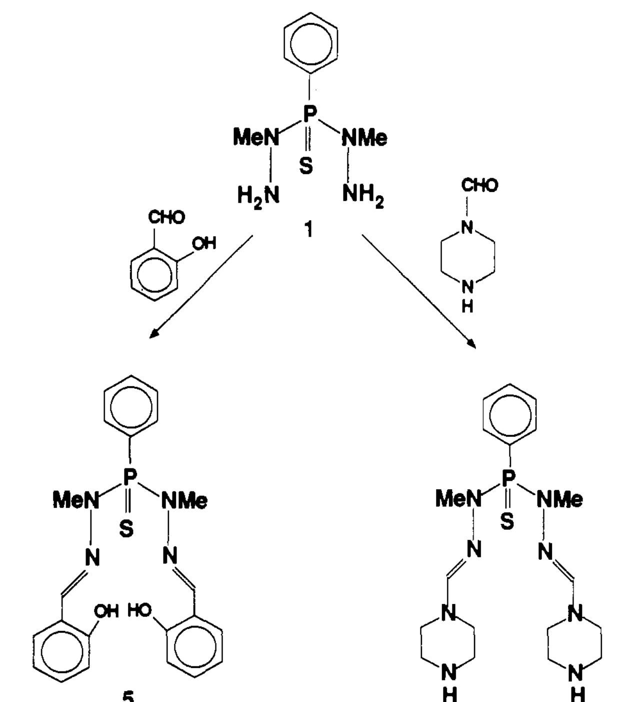


Figure 2. ORTEP drawing of the molecular structure of compound **7** with 50% thermal ellipsoids.

Scheme III



substituents attached to the terminal nitrogens, we see a considerable elongation in the P=S bond (2.279 Å) in **7** compared to the same bond (1.935 Å) in a closely related free phosphorus hydrazide ligand **1**.[19]

The donor properties of Ph$_3$P=S and Ph$_3$P=Se are generally weaker compared to Ph$_3$P=O; however, the Pd(II) complexes of all these three phosphorus chalcogenides are known and are in the form of PdX$_2$L$_2$ (X = Cl, Br; L = Ph$_3$P(S), Ph$_3$P(Se)).[20] All these complexes are highly insoluble and show hydrolytic instability. The phosphohydrazide Pd(II) complexes **4**, **7**, and **8** are some of the rare examples of compounds involving phosphine sulfide–palladium(II) bonding which are hydrolytically very robust; presumably, this is a consequence of strong chelate interactions involving highly basic hydrazine nitrogens and the strong Pd–S bonds within the metallocyclic formulation.

(19) Katti, K. V.; Pinkerton, A. Unpublished Results.

Scheme IV

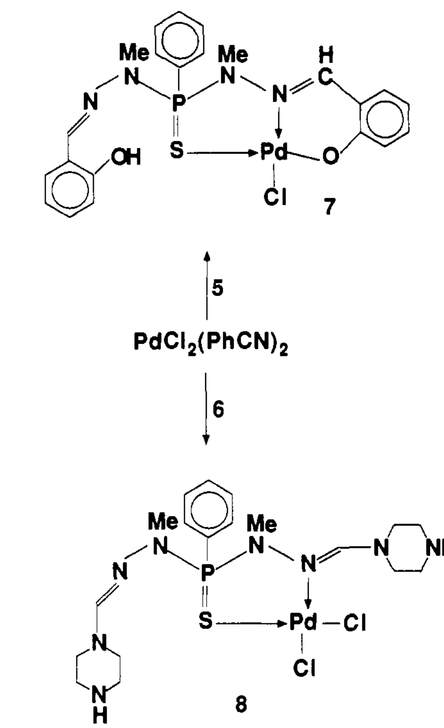


Table VI. Selected Bond Length and Bond Angle Data for **7**

	Bond Lengths (Å)		
Pd–Cl	2.3041 (13)	O1–C1	1.285 (5)
Pd–S	2.2798 (12)	C7–N1	1.302 (5)
Pd–O1	1.988 (3)	N1–N2	1.414 (4)
Pd–N1	2.001 (3)	N2–C8	1.460 (6)
S–P	1.9823 (17)	N3–C9	1.453 (6)
P–N2	1.668 (3)	N3–N4	1.402 (4)
P–N3	1.653 (3)	N4–C10	1.279 (5)
P–C17	1.788 (5)		
	Bond Angles (deg)		
Cl–Pd–S	86.78 (5)	Pd–O1–C1	125.4 (3)
Cl–Pd–O1	87.63 (10)	Pd–N1–C7	124.1 (3)
Cl–Pd–N1	177.99 (10)	Pd–N1–N2	118.20 (24)
S–Pd–O1	173.96 (10)	C7–N1–N2	117.6 (3)
S–Pd–N1	92.20 (10)	P–N2–N1	113.9 (3)
O1–Pd–N1	93.46 (13)	P–N2–C8	122.4 (3)
Pd–S–P	94.52 (6)	N1–N2–C8	119.4 (3)
S–P–N2	107.19 (13)	P–N3–C9	119.5 (3)
S–P–N3	114.01 (14)	P–N3–N4	114.7 (3)
S–P–C17	114.69 (16)	C9–N3–N4	120.3 (3)
N2–P–N3	102.84 (17)	N3–N4–C10	118.7 (3)
N2–P–C17	109.89 (19)	N4–C10–C11	119.9 (4)
N3–P–C17	107.54 (18)		

Infrared and NMR Spectroscopic Trends of the Free Phosphorus Hydrazide Ligands and Their Metal Complexes. The IR stretching frequency of the NH$_2$ group in the free hydrazide ligand **1** consisted of bands at 3264 and 3163 cm^{-1} ascribed to asymmetric and symmetric NH$_2$ stretching modes (Table V). A significant lowering of the wave numbers for the ν(NH$_2$) stretching frequency occurred upon complexation e.g., ν(NH$_2$) for **2**, **3**, and **4** was 120–130 cm^{-1} lower compared to that for **1**. The observation of two ν(NH$_2$) bands at 3250 and 3052 cm^{-1} is diagnostic of the presence of free and coordinated N–NH$_2$ groups in **4**. Perchlorate

(20) Lobana, T. S.; Sharma, K. *Transition Met. Chem. (Weinheim, Ger.)* **1982**, *7*, 133 and references therein.

bands at 1080 (broad) and 620 cm^{-1} observed in **2** and **3** are consistent with the uncoordinated perchlorate ion. Comparison of the ν(P=S) stretching frequency of the free ligands **1**, **5**, and **6** with those of the corresponding Co(I), Cu(I), and Pd(II) complexes proved to be diagnostic of the metal coordination with the P=S unit. The ν(P=S) in **1**, **5**, and **6** consisted of an intense band in the 600–610-cm^{-1} region, and this band moved to lower wave numbers by 65–75 cm^{-1} in all of the metal complexes **2**, **3**, **4**, **7**, and **8**. This observation is consistent with the single bond formulation of the P=S unit in all these complexes as confirmed by our X-ray crystallographic analysis of **2** and **7**. The IR spectroscopic data for the ν(P=S) and the P=S bond lengths of 1.977 and 1.982 Å (Tables IV and VI) for **2** and **7** respectively, strongly support a charge distribution type of bonding model (i.e., P^+–S^-) for the P=S bond in all of these metal complexes.

In the ^{1}H NMR spectra, the N–CH_3 protons of the free ligands **1**, **5**, and **6** resonated as a clear sharp doublet as a result of coupling with the phosphorus across three bonds (^3J(P–H) = 9–12 Hz) (Table V). The ^{1}H NMR spectrum showed a single doublet for the N–CH_3 groups (^3J(P–H) = 12.0 Hz), and this observation supports the structure of **2** wherein all four N–CH_3 groups are equivalent and all four –NH_2 groups around the Co(I) center are intact. The deprotonation of one or more of the hydrazine arms would cause chemical inequivalencies of the –N–CH_3 groups and result in multiple doublets. There was a modest, deshielding of this signal upon complexation as observed for **4**, **7**, and **8** (Table V); however, the presence of an additional N–CH_3 signal whose chemical shift is very close or identical to those found in the corresponding free ligands suggests that only one arm of the hydrazine unit is involved in the bonding with the Pd(II) center as formulated for all these complexes. The upfield chemical shifts δ 2.75, 3.21, and 3.18 and the downfield chemical shifts δ 3.24, 3.40, and 3.50 in **4**, **7**, and **8** have been assigned to the NCH_3 protons present in the free and the coordinated hydrazine units respectively.

The ^{31}P NMR spectrum of **2** showed a sharp, single resonance line at 88.5 ppm indicating a diamagnetic species. The ^{31}P NMR spectra of the free ligands **1**, **5**, and **6** and their metal complexes **4**, **7**, and **8** consisted of single sharp resonances (Table V), indicating the presence of single chemical species. There is only a modest deshielding of the ^{31}P chemical shifts (by 2–4 ppm) on going from the free ligands to the metal complexes (Table V). The ^{31}P NMR chemical shift behavior of **4**, **7**, and **8**, which have the P–N–N–M skeleton, is in sharp contrast to the observations of chemical shifts noted in phosphinaminato complexes which have P–N–M skeleton(s). Phosphinaminato (P–N–M) complexes of early and late transition metals have been reported to show a magnitude of deshielding of 20–30 ppm compared to the free phosphinamino ligands;[21–23] presumably a consequence of the disposition of the metal center two bonds away from the phosphorus as compared to three bonds away from phosphorus in cyclometallaphosphohydrazides **4**, **7**, and **8** and, hence, a more efficient electronic charge withdrawal effect in the former than in the latter set of compounds.

In summary, a new mode of coordination involving hydrazide and phosphorus sulfide functionalities with different transition metals has been established. Compounds **2**, **3**, **4**, **7**, and **8** have very high kinetic stabilities and can be used as model systems to generate hydrazide complexes of early transition metals such as Mo, W, and Re. The facile incorporation of different organic functionalities on the ligand backbones (Scheme III) is unique and demonstrates a synthetic methodology to develop the transition metal chemistry of functionalized ligand systems.

Acknowledgment. We gratefully acknowledge the support of the National Science Foundation, Grant No. CHE[90-11804], for partial funding of the X-ray diffractometer. We also thank Dr. Wynn A. Volkert and Dr. Alan R. Ketring for helpful discussions. P.R.S. thanks Dr. D. E. Troutner for financial support.

Supplementary Material Available: Full tables of crystallographic data, bond lengths and bond angles, fractional coordinates and isotropic temperature parameters for hydrogen atoms, and anisotropic thermal parameters for other atoms (9 pages). Ordering information is given on any current masthead page.

(21) (a) Katti, K. V.; Cavell, R. G. *Organometallics* **1991**, *10*, 539. (b) Katti, K. V.; Cavell, R. G. *Organometallics* **1988**, *7*, 2236. (c) Katti, K. V.; Cavell, R. G. *Inorg. Chem.* **1989**, *28*, 413. (d) Katti, K. V.; Cavell, R. G. *Organometallics* **1989**, *8*, 2147. (e) Katti, K. V.; Cavell, R. G. *Comments Inorg. Chem.* **1990**, *10*, 53.
(22) Dehnicke, K.; Strähle, J. *Polyhedron* **1989**, *8*, 707 and references therein.
(23) (a) Katti, K. V.; Seseke, U.; Roesky, H. W. *Inorg. Chem.* **1987**, *26*, 814. (b) Roesky, H. W.; Katti, K. V.; Seske, U.; Witt, M.; Egert, R.; Herbst, R.; Sheldrick, G. M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 477.