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Transition Metal Chemistry of Main Group Hydrazides. 16. (Phosphanyl)hydrazines $R_2PN(Me)N(Me)PR_2$ as a Novel Class of Chelating Bis(phosphines). Synthesis, Coordination Chemistry, and X-ray Structures of *cis*-$[PdCl_2\{(p\text{-}BrC_6H_4O)_2PN(Me)N(Me)P(OC_6H_4Br\text{-}p)_2\}]$ and *cis*-$[W(CO)_4\{(PhO)_2PN(Me)N(Me)P(OPh)_2\}]$

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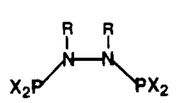
The alkoxy- and aryloxy-functionalized bis(phosphanyl)hydrazines of the type $(OR)_2PN(Me)N(Me)P(OR)_2$ were obtained from the reactions of the corresponding alcohols and phenols with $Cl_2PN(Me)N(Me)PCl_2$ in the presence of Et_3N. Interaction of these ligands with group 6 metal carbonyl precursors $M(CO)_4(NHC_5H_{10})_2$ (M = Mo, W) gave the tetracarbonyl complexes of the type *cis*-$[M(CO)_4(OR)_2PN(Me)N(Me)P(OR)_2\}]$. The reactions of the alkoxy and aryloxy−functionalized bis(phosphanyl)hydrazines with $Pd(PhCN)_2Cl_2$ or with $Pt(COD)Cl_2$ resulted in the formation of the complexes of the type *cis*-$[MCl_2(OR)_2PN(Me)N(Me)P(OR)_2\}]$. The ligands are bound *cis* to the metal center(s) in all the complexes. The structures of all the complexes have been established by combination of spectroscopic and elemental analysis. As representative examples, we have determined the structures of *cis*-$[W(CO)_4\{(OPh)_2PN(Me)N(Me)P(OPh)_2\}]$ (**15**) and *cis*-$[PdCl_2\{(OC_6H_4Br\text{-}p)_2PN(Me)N(Me)P(OC_6H_4Br\text{-}p)_2\}]$ (**19**) by X-ray crystallography. X-ray data for **15**: monoclinic, $P2_1/n$, $a = 13.419(5)$ Å, $b = 19.588(3)$ Å, $c = 12.253(3)$ Å, $\beta = 103.65(2)°$, $Z = 4$, and $R = 0.025$ ($R_w = 0.033$). X-ray data for **19**: triclinic, $P\bar{1}$, $a = 9.252(3)$ Å, $b = 9.882(3)$ Å, $c = 17.739(5)$ Å, $\alpha = 83.84(2)°$, $\beta = 83.98(2)°$, $\gamma = 84.45(2)°$, $Z = 2$, and $R = 0.064$ ($R_w = 0.076$).

Introduction

The discovery of new chelating bis(phosphines) continues to attract considerable attention because of their role in the development of catalytically useful transition metal complexes.[1−5] Among the alkane-bridged bis(phosphines), (*e.g.*, $R_2P(CH_2)_n$)-PR_2) bis(di(alkyl or aryl)phosphino)ethane has found numerous applications in the design of monometallic-based transition metal compounds and catalysts.[1,6] The appropriate bite angle provided by the ethane backbone has been implicated as the main reason for the prevalence of stable five-membered mononuclear chelates with demonstrated catalytic properties.[1,6] The development of new bis(phosphines) that possess similar spacing between the P^{III} centers, as in $R_2P(CH_2)_2PR_2$, may present the potential to expand the scope of the transition metal chemistry of chelating bis(phosphines). In this connection, the ethylene-bridged bis(phosphine) $R_2PCH{=}CHPR_2$ has provided an interesting example of a ligand with a similar chain length as that of diphos. We have reasoned that the development of bis(phosphines) with main group centers (*e.g.* nitrogen) connecting the P^{III} centers may offer new opportunities in tuning the electronic and steric characteristics of the interacting phosphines. Towards this objective the discovery of a novel synthetic strategy to bis(dichlorophosphino)dimethylhydrazine ($Cl_2PN(Me)N(Me)PCl_2$) was recently reported.[7,8] This dinitrogen-bridged bis(phosphine), **1**, is a useful synthon, because (a) it has a similar chain length as that of diphos suggesting its utility in the formation of mononuclear five-membered chelates[9] and (b) the reactive chlorides may be used in the development of a wide spectrum of $R_2PN(Me)N(Me)PR_2$-type of derivatives affording systematic tuning of nucleophilicity and π-acidity of the P^{III} centers.[9,10] It may also be noted that the development of fundamental coordination chemistry of hydrazine−bridged bis(phosphines) (**A**) may aid in furthering the chemistry of the higher homologue of bis(phosphino)amines (**B**).[11] In this paper we report the synthesis and characterization of a series of bis(phosphanyl)hydrazines ($R_2PN(Me)N(Me)PR_2$). The coordination chemistry of these new phosphanyl hydrazines with Mo(0), W(0), Pd(II) and Pt(II) precursors is also described through the X-ray structural analysis of the representative examples.



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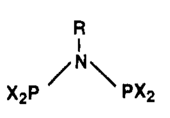

B

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Experimental Section

All reactions were carried out under purified nitrogen by standard Schlenk techniques. Solvents were purified and dried by standard methods and distilled under nitrogen prior to use. Reagents such as dimethylhydrazine dihydrochloride, PCl_3, MeOH, EtOH, CF_3CH_2OH, $CH_2{=}CHCH_2OH$, $CH_3(CH_2)_7OH$, *i*-PrOH, *p*-BrC_6H_4OH, $[Mo(CO)_4(NHC_5H_{10})_2]$, $PdCl_2(PhCN)_2$, and $PtCl_2(COD)$ were purchased from Aldrich Chemical Co. and were used without further purification. $[W(CO)_4(NHC_5H_{10})_2]$ was prepared by literature methods.[12] The compound $[Cl_2PN(Me)N(Me)PCl_2]$ (**1**) was prepared by refluxing 1,2-dimethylhydrazine dihydrochloride in large excess PCl_3.[8] Triethylamine was distilled over KOH and stored over molecular sieves under N_2.

Nuclear magnetic resonance spectra were recorded on Bruker AMX-500 and ARX-300 spectrometers using $CDCl_3$ solvent. The ^1H NMR chemical shifts are reported in 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 chemical shifts lie downfield of the standard. Infrared spectra were recorded using Nujol mulls and KBr cells on a Mattson Galaxy 3000 spectrophotometer. Elemental analyses were performed by Onida Research Services, Inc. New York.

General Procedure for $(RO)_2PN(Me)N(Me)P(OR)_2$ (2–8). A mixture of corresponding alcohol (82.0 mmol) and Et_3N (84.0 mmol) in *n*-hexane (50 mL) was added dropwise to **1** (20.5 mmol) also in hexane (200 mL) at 25 °C. The reaction mixture was stirred for 2 h, and the $Et_3N{\cdot}HCl$ was filtered off. Removal of the solvent *in vacuo* gave the analytically pure title compound(s) in 75–90% yield as a viscous liquid(s).

R = Me (2). Yield: 76% (3.7 g). Anal. Calcd for $C_6H_{18}N_2O_4P_2$: C, 29.51; H, 7.43; N, 11.47. Found: C, 29.72; H, 7.61; N, 11.19. ^1H NMR: δ 2.78 (t, $^3J_{PH} + {}^4J_{PH} = 1.7$ Hz, 6H, NCH_3), 3.50 (t, $J_{PH} = 6.8$ Hz, 12H, OMe), ^{31}P NMR: δ 148.5 (s).

R = Et (3). Yield 78% (4.7 g). Anal. Calcd for $C_{10}H_{26}N_2O_4P_2$: C, 40.00; H, 8.73; N, 9.33. Found: C, 40.12; H, 8.57; N, 9.42. ^1H NMR: δ 2.98 (t, $^3J_{PH} + {}^4J_{PH} = 1.7$ Hz, 6H, NCH_3), 1.27 (t, $J_{PH} = 7.0$ Hz, 12H, CH_3), 3.90 (m, br, 8H, OCH_2). ^{31}P NMR: δ 139.9 (s).

R = CH_2CF_3 (4). Yield: 86% (8.9 g). Anal. Calcd for $C_{10}H_{14}F_{12}N_2O_4P_2$: C, 23.27; H, 2.73; N, 5.43. Found: C, 23.28; H, 2.68; N, 5.36. ^1H NMR: δ 2.85 (t, $^3J_{PH} + {}^4J_{PH} = 2.4$ Hz, 6H, NCH_3), 4.10 (m, br, 8H, OCH_2). ^{31}P NMR: δ 147.3 (s).

R = $CH_2CH{=}CH_2$ (5). Yield: 82% (5.7 g). Anal. Calcd for $C_{14}H_{26}N_2O_4P_2$: C, 48.26; H, 7.53; N, 8.04. Found: C, 47.72; H, 7.62; N, 8.41. ^1H NMR: δ 2.93 (t, $^3J_{PH} + {}^4J_{PH} = 1.7$ Hz, 6H, NCH_3), 4.35 (m, 8H, OCH_2), 5.25 (m, 8H, $CH{=}CH_2$), 5.93 (m, 4H, $CH{=}CH_2$). ^{31}P NMR: δ 142.3 (s).

R = $(CH_2)_7CH_3$ (6). Yield: 74% (9.4 g). Anal. Calcd for $C_{34}H_{74}N_2O_4P_2$: C, 64.12; H, 11.71; N, 4.40. Found: C, 63.85; H, 11.43; N, 4.59. ^1H NMR: δ 0.81 (t, $^3J_{HH} = 13.4$ Hz, 12H, CH_2CH_3), 1.20 (m, br, 40H, $(CH_2)_5CH_3$), 1.53 (m, br, 8H, OCH_2CH_2), 2.68 (t, $^3J_{PH} + {}^4J_{PH} = 1.7$ Hz, 6H, NCH_3), 3.62 (m, 8H, OCH_2). ^{31}P NMR: δ 143.1 (s).

R = $CH(CH_3)_2$ (7). Yield: 80% (5.7 g). Anal. Calcd for $C_{14}H_{36}N_2O_4P_2$: C, 46.92; H, 10.13; N, 7.82. Found: C, 46.63; H, 10.19; N, 7.57. ^1H NMR: δ 1.25 (t, $^3J_{HH} + {}^4J_{PH} = 6.8$ Hz, 12H, $CH(CH_3)_2$), 2.72 (t, $^3J_{PH} + {}^4J_{PH} = 1.0$ Hz, 6H, NCH_3), 4.22 (m, br, 4H, OCH). ^{31}P NMR: δ 143.0 (s).

R = C_6H_4Br-*p* (8). Yield: 87% (14.0 g). Anal. Calcd for $C_{26}H_{22}Br_4N_2O_4P_2$: C, 38.65; H, 2.74; N, 3.47. Found: C, 38.57; H, 2.81; N, 3.41. ^1H NMR: δ 2.92 (t, $^3J_{PH} + {}^4J_{PH} = 2.50$ Hz, 6H, NCH_3), 6.8–7.5 (m, 16H, C_6H_4). ^{31}P NMR: δ 138.0 (s).

The aryloxy derivatives of **1** (R = OPh, **9** and R = $OC_6H_4(CH_2CH{=}CH_2)$, **10**) were prepared according to previously published procedures.[9]

$Ph_2PN(Me)N(Me)Ph_2$ (11). To a solution of **1** (5.0 g, 19.08 mmol) in THF (50 mL) was added dropwise a solution of PhMgCl (78.0 mmol) also in THF (150 mL) at 0 °C with constant stirring. Stirring was continued for further 4 h while allowing the reaction mixture to warm to room temperature. The magnesium chloride was filtered off, the solution was concentrated to ~50 mL *in vacuo*, and ~50 mL of *n*-hexane was added. The resulting solution was cooled at 0 °C for 8 h, to afford the white crystalline powder of **11** in 85% (8.2 g) yield. Anal. Calcd for $C_{26}H_{26}N_2P_2$: C, 72.89; H, 6.12; N, 6.54. Found: C, 72.46; H, 5.98; N, 6.64. ^1H NMR: δ 2.70 (t, $^3J_{PH} + {}^4J_{PH} = 1.10$ Hz, 6H, NCH_3), 7.3 (m, 20H, Ph). ^{31}P NMR: δ 62.5 (s).

***cis*-$[Mo(CO)_4\{(OR)_2PN(Me)N(Me)P(OR)_2\}]$ (R = CH_2CF_3 (12), Ph (13)).** To a solution of *cis*-$[Mo(CO)_4(NHC_5H_{10})_2]$ (0.529 mmol) in dichloromethane (25 mL) was added dropwise at 25 °C a solution of the corresponding ligand (**4** or **9**) (0.540 mmol) also in dichloromethane (25 mL). The reaction mixture was heated under reflux for 2 h before the solvent was removed *in vacuo* to obtain a yellow microcrystalline powder. This residue was extracted from a mixture of CH_2Cl_2/hexane (1:1 ratio), and the extracts (3 × 10 mL) were filtered through a column of silica gel (20 g). Evaporation of the solvent *in vacuo* gave the title compound(s) **12** and **13** as an yellow crystalline solid(s).

R = CH_2CF_3, (12). Yield 78% (0.30 g). Anal. Calcd for $C_{14}H_{14}F_{12}N_2O_8P_2Mo$: C, 23.22; H, 1.95; N, 3.87. Found: C, 23.20; H, 1.89; N, 3.92. IR (Nujol) (ν (CO)): 2057 (sh), 1972 (s), 1951 (s), and 1912 (vs) cm^{-1}. ^1H NMR: δ 2.83 (t, $^3J_{PH} + {}^4J_{PH} = 2.4$ Hz, 6H, NCH_3), 4.20 (m, 8H, OCH_2). ^{31}P NMR: δ 194.0 (s).

R = Ph (13). Yield 80% (0.30 g). Anal. Calcd for $C_{30}H_{26}N_2O_8P_2Mo$: C, 51.44; H, 3.74; N, 4.00. Found: C, 51.42; H, 3.79; N, 4.05. IR (Nujol) (ν (CO)): 2037 (s), 1952 (s), 1935 (s), and 1921 (vs) cm^{-1}. ^1H NMR: δ 3.00 (t, $^3J_{PH} \bullet {}^4J_{PH} = 3.8$ Hz, 6H, NCH_3), 7.0–7.45 (m, 20H, OPh). ^{31}P NMR: δ 172.6 (s).

***cis*-$[W(CO)_4\{(OR)_2PN(Me)N(Me)P(OR)_2\}]$ (R = CH_2CF_3 (14), Ph (15)).** To a solution of *cis*-$[W(CO)_4(NHC_5H_{10})_2]$ (1.00 mmol) in dichloromethane (25 mL) was added dropwise at 25 °C a solution of the corresponding ligand (**4** or **9**) (1.00 mmol) also in dichloromethane (25 mL). The reaction mixture was heated under reflux for 6 h and worked up as described above for **12** and **13** to obtain the title compound(s) as yellow microcrystalline powders.

R = CH_2CF_3 (14). Yield: 76% (0.64 g). Anal. Calcd for $C_{14}H_{14}F_{12}N_2O_8P_2W$: C, 20.71; H, 1.74; N, 3.45. Found: C, 21.04; H, 1.86; N, 3.39. IR (Nujol) (ν (CO)): 2052 (sh), 1965 (s), 1994 (s), and 1904 (vs) cm^{-1}. ^1H NMR: δ 2.82 (t, $^3J_{PH} + {}^4J_{PH} = 3.8$ Hz, 6H, NCH_3), 4.40 (m, 8H, OCH_2). ^{31}P NMR: δ 173.9 (s, $^1J_{WP} = 366$ Hz).

R = Ph (15). Yield 82% (0.65 g). Anal. Calcd for $C_{30}H_{26}N_2O_8P_2W$: C, 45.71; H, 3.32; N, 3.55. Found: C, 45.74; H, 3.36; N, 3.51. IR (Nujol) (ν (CO)): 2033 (sh), 1944 (s), 1927 (s), and 1914 (vs) cm^{-1}. ^1H NMR: δ 2.98 (t, $^3J_{PH} + {}^4J_{PH} = 4.0$ Hz, 6H, NCH_3), 7.1–7.5 (m, 20H, OPh). ^{31}P NMR: δ 169.3 (s, $^1J_{WP} = 373$ Hz).

General Procedure for Palladium Complexes *cis*-$[PdCl_2\{(OR)_2PN(Me)N(Me)P(OR)_2\}]$ (R = CH_2CF_3 (16), *i*-Pr (17), Ph (18), C_6H_4Br-*p*, (19), $C_6H_4(2\text{-}CH_2CH{=}CH_2)$ (20)). A dichloromethane solution of the corresponding ligand (0.800 mmol) was added dropwise to a solution of $PdCl_2(PhCN)_2$ (0.785 mmol) also in dichloromethane (25 mL) at 25 °C. The reaction mixture was stirred for 0.5 h before the solvent was removed *in vacuo* to obtain yellow microcrystalline powder. This was washed with hexane to remove the benzonitrile and dried *in vacuo* to obtain the title complex(s) in 90–95% yield.

R = CH_2CF_3 (16). Yield: 91% (0.50 g). Anal. Calcd for $C_{10}H_{14}Cl_2F_{12}N_2O_4P_2Pd$: C, 17.32; H, 2.03; N, 4.04. Found: C, 17.42; H, 2.16; N, 3.91. ^1H NMR: δ 2.94 (t, $^3J_{PH} + {}^4J_{PH} = 5.2$ Hz, 6H, NCH_3), 4.42 (m, br, 8H, OCH_2). ^{31}P NMR: δ 126.4 (s).

R = $CH(CH_3)_2$ (17). Yield: 94% (0.60 g). Anal. Calcd for $C_{14}H_{36}Cl_2N_2O_4P_2Pd$: C, 31.39; H, 6.77; N, 5.23. Found: C, 31.48; H, 6.85; N, 5.02. ^1H NMR: δ 1.40 (dd, $^3J_{HH} = 5.9$ Hz, $^4J_{PH} = 4.4$ Hz, 12H, $CH(CH_3)_2$), 2.76 (t, $^3J_{PH} + {}^4J_{PH} = 5.2$ Hz, 6H, NCH_3), 5.40 (m, br, 4H, $CH(CH_3)_2$). ^{31}P NMR: δ 120.7 (s).

R = C_6H_5 (18). Yield: 87% (0.67 g). Anal. Calcd for $C_{26}H_{22}Br_4Cl_2N_2O_4P_2Pd$: C, 31.69; H, 2.25; N, 2.84. Found: C, 31.72; H, 2.21; N, 2.67. ^1H NMR: δ 2.92 (t, $^3J_{PH} + {}^4J_{PH} = 5.0$ Hz, 6H, NCH_3), 7.0–7.5 (m, 16H, C_6H_4). ^{31}P NMR: δ 118.4 (s).

R = $C_6H_4(2\text{-}CH_2CH{=}CH_2)$ (20). Yield: 90% (0.60 g). Anal. Calcd for $C_{38}H_{42}Cl_2N_2O_4P_2Pd$: C, 54.99; H, 5.10; N, 3.37. Found: C, 55.27; H, 5.23; N, 3.19. ^1H NMR: δ 2.90 (t, $^3J_{PH} + {}^4J_{PH} = 4.8$ Hz, NCH_3), 3.45 (*ABX* pattern, $^2J_{HAHB} = 15.9$ Hz, $^3J_{HAHX} = 6.3$ Hz, 8H, $C_6H_4CH_2CH$), 5.0 (*AMX* pattern, $^3J_{HXHM} = 16.5$ Hz, $^3J_{HXHA} = 10.1$ Hz, $^2J_{HAHM} = 0.8$ Hz, 8H, $CH{=}CH_2$), 5.90 (m, 4H, $CH_2CH{=}CH_2$), 7.07–7.30 (m, 16H, C_6H_4). ^{31}P NMR: δ 104.1 (s).

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Table 1. Crystal Data for Complexes **15** and **19**

	15	**19**
formula	$C_{30}H_{26}N_2O_8F_{12}P_2W$	$C_{26}H_{16}N_2O_4P_2Cl_2Br_4Pd$
crystal system	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$
fw	788.33	979.28
a, Å	13.419(5)	9.252(3)
b, Å	19.588(3)	9.882(3)
c, Å	12.253(3)	17.739(5)
α, deg	90.0	83.74(2)
β, deg	103.65(2)	83.98(2)
γ, deg	90.0	84.45(2)
Z	4	2
$F(000)$	1552	934
V, Å^3	3129.8(2)	1597.3(8)
d_{calc}, g/cm^3	1.673	2.036
cryst size, mm	0.20 × 0.35 × 0.40	0.05 × 0.15 × 0.25
μ, mm^{-1}	3.92	5.83
no. of unique rflns	4332	3909
no. of reflns with $I > 2\sigma(I)$	3669	2352
no. of variables	388	240
R; R_w[a]	0.025; 0.033	0.064; 0.076
GOF	1.08	2.01
max shift/σ	0.002	0.006
res. electron density, e/Å^3	0.39	1.51

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

General Procedure for Platinum Complexes: *cis*-[$PtCl_2\{(RO)_2PN(Me)N(Me)P(OR)_2\}$] (R = CH_2CF_3 (21), *i*-Pr (22), $(CH_2)_7CH_3$ (23), C_6H_4Br-*p* (24)). A dichloromethane solution of the corresponding ligand (0.830 mmol) was added dropwise to a solution of $PtCl_2(COD)$ (0.806 mmol) also in dichloromethane (25 mL) at 25 °C. The reaction mixture was stirred for 2 h, and the solvent was removed *in vacuo* to obtain white microcrystalline powder(s). This was washed from *n*-hexane to remove the cyclooctadiene and dried *in vacuo* to obtain the title complex(s) in 90−95% yield.

R = CH_2CF_3 (21). Yield: 91% (0.57 g). Anal. Calcd for $C_{10}H_{14}Cl_2F_{12}N_2O_4P_2Pt$: C, 15.36; H, 1.80; N, 3.58. Found: C, 15.43; H, 1.92; N, 3.47. ^{1}H NMR: δ 2.92 (dd, $^3J_{PH} = 7.6$ Hz, $^4J_{PH} = 2.0$ Hz, 6H, NCH_3), 4.80 (m, br, 8H, OCH_2). ^{31}P NMR: δ 103.6 (s, $^1J_{PtP} = 5362$ Hz).

R = $CH(CH_3)_2$ (22). Yield: 96% (0.48 g). Anal. Calcd for $C_{14}H_{36}Cl_2N_2O_4P_2Pt$: C, 26.93; H, 5.81; N, 4.49. Found: C, 27.21; H, 5.99; N, 4.37. ^{1}H NMR: δ 1.40 (dd, $^3J_{HH} = 7.6$ Hz, $^4J_{PH} = 2.0$ Hz, 12H, $CH(CH_3)_2$), 2.76 (t, $^3J_{PH} + {}^4J_{PH} = 2.9$ Hz, 6H, NCH_3), 4.95 (m, 4H, $CH(CH_3)_2$). ^{31}P NMR: δ 94.8 (s, $^1J_{PtP} = 5412$ Hz).

R = $(CH_2)_7CH_3$ (23). Yield: 94% (0.68 g). Anal. Calcd for $C_{34}H_{74}Cl_2N_2O_4P_2Pt$: C, 45.23; H, 8.26; N, 3.10. Found: C, 45.01; H, 8.13; N, 2.98. ^{1}H NMR: δ 0.88 (t, $^3J_{HH} = 13.2$ Hz, 12H, CH_2CH_3), 1.27 (m, br, 40H, $(CH_2)_5CH_3$), 1.71 (m, br, 8H, OCH_2CH_2), 2.87 (t, $^3J_{PH} + {}^4J_{PH} = 4.8$ Hz. 6H, NCH_3), 4.40 (m, 8H, OCH_2). ^{31}P NMR: δ 99.7 (s, $^1J_{PtP} = 5384$ Hz).

R = C_6H_4Br-*p* (24). Yield: 97% (0.84 g). Anal. Calcd for $C_{26}H_{22}Br_4Cl_2N_2O_4P_2Pt$: C, 29.08; H, 2.06; N, 2.61. Found: C, 29.12; H, 2.10; N, 2.78. ^{1}H NMR: δ 2.92 (t, $^3J_{PH} + {}^4J_{PH} = 5.0$ Hz, 6H, NCH_3), 7.1−7.4 (m, 16H, C_6H_4). ^{31}P NMR: δ 95.4 (s, $^1J_{PtP} = 5408$ Hz).

X-ray Data Collection and Processing

The crystal data and details of data collection for **15** and **19** are listed in Table 1. Yellow crystals of **15** suitable for X-ray diffraction were obtained from CH_2Cl_2/hexane (1:3 v/v) at 0 °C, whereas suitable crystals of **19** were obtained by slow evaporation of its $CDCl_3$ solution. All X-ray data were collected on an Enraf-Nonius CAD-4 diffractometer with Mo Kα radiation and a graphite monochromator at 22(1) °C. The cell dimensions were obtained from a least-squares fit to setting angles of 25 reflections with 2θ in the range 20.0−30.0°. Crystals of **15** and **19** exhibited no significant decay under X-ray irradiation.

The structures were solved by direct methods and were subsequently refined by the full-matrix least square method which minimizes $\sum w(|F_o| - |F_c|)^2$ where $w^{-1} = [\sigma(\text{counting}) + (0.008(F_o)^2)/4F_o]$. Atomic scattering factors which included anomalous scattering contributions were from ref 13. All hydrogen atoms in both structures were located in difference Fourier maps and refined with fixed isotropic thermal parameters. The final cycle of the least-squares refinement gave an agreement factor R of 0.025 for **15** and 0.064 for **19**. The programs used for the crystallographic computations are reported in ref 14.

Results and Discussion

Synthesis of Bis(phosphanyl)hydrazines. The alkoxy- and aryloxy-functionalized dinitrogen-bridged bis(phosphanes) $(RO)_2PN(Me)N(Me)P(OR)_2$ (R = Me (**2**), Et (**3**), CH_2CF_3 (**4**), $CH_2CH{=}CH_2$ (**5**), $(CH_2)_7CH_3$ (**6**), $CH(CH_3)_2$ (**7**), C_6H_4Me-*p* (**8**) were obtained from the reactions of the corresponding alcohols or phenols with $Cl_2PN(Me)N(Me)PCl_2$ (**1**) in the presence of Et_3N in 75−90% yields (Scheme 1). The phenyl derivative, $Ph_2PN(Me)N(Me)PPh_2$ (**11**) was synthesized by the reaction of a Grignard reagent, PhMgCl, with **1**, in THF solution in 85% yield. All the alkoxide (**2**−**7**) and aryloxide (**8**−**10**) derivatives are air-stable, colorless, viscous liquids, whereas the phenyl derivative is a white crystalline powder and is somewhat hygroscopic. Previous studies have described the preparation of the phenyl derivative by the condensation reaction of *N,N'*-dimethylhydrazine and PPh_2Cl at −196 °C.[15] All the above ligands have been characterized by various spectroscopic and analytical methods. The ^{31}P NMR spectra of all the compounds consisted of single resonance(s) in the range between 137−148 ppm for alkoxide and aryloxides and at 62.5 ppm for the phenyl derivative **11** (Table 2). The ^{1}H NMR data for **2**−**11** are consistent with the proposed structures. The ^{1}H NMR spectra of all the compounds (**2**−**8**) show a triplet in the region 2.7−3.0 ppm due to the NCH_3 protons with small coupling constants of 1.0−2.5 Hz, with apparent "virtual coupling", for both the phosphorus nuclei.

Coordination Chemistry of Bis(phosphanyl)hydrazines. Interaction of $M(CO)_4(NHC_5H_{10})_2$ (M = Mo and W) with diphosphane ligands **4** and **9** afford the mononuclear tetracarbonyl complexes of the type *cis*-[$M(CO)_4\{(RO)_2PN(Me)N(Me)P(OR)_2\}$] (M = Mo, R = CH_2CF_3 (**12**), Ph (**13**); M = W, R = CH_2CF_3 (**14**), Ph (**15**) (Scheme 2). The ligands are bound *cis* to the metal center(s) in all the complexes (**12**−**15**) as inferred by infrared spectroscopy. ^{31}P NMR chemical shifts of all the complexes (**12**−**15**) show single resonances (Table 2) and indicate the equivalence of both the phosphorus nuclei. The observation of a large downfield shift in the molybdenum complex is consistent with other Mo(0) complexes reported in the literature.[11] The down-field shift in both the tungsten complexes, **14** (32.3 ppm) and **15** (26.6 ppm) is in contrast to the general trends observed for the tungsten complexes of diphosphinoamine and diphosphazane ligands[11] for which the reasons are not clear. The large coupling constant values for $^1J_{WP}$ (366 Hz for **14** and 373 Hz for **15**) indicate the strong W−P interactions, as indicated in their short W−P bond distances observed in the structure of **15** (Table 3). ^{1}H NMR spectroscopic data for of all the complexes are consistent with the proposed structures for **12**−**15**. Observation of triplets for the NCH_3 protons, between 2.8 and 3.0 ppm with relatively

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(13) *International Tables For X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. 4.

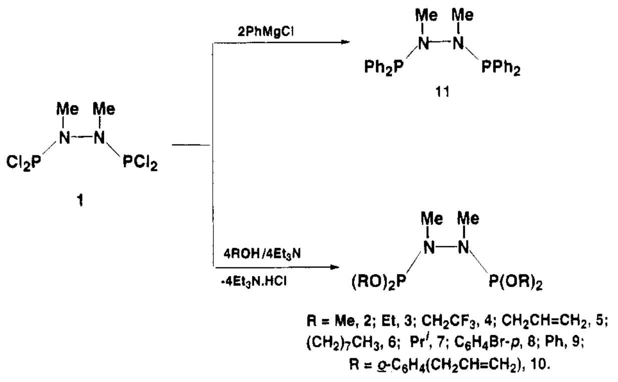
(14) The following references are relevant to the NRCVAX system: (a) Gabe, E. J.; Page, Y. L.; Charland, J. L.; Lee, F. L.; White, P. S. *J. Appl. Crystallogr.* **1989**, *22*, 384. (b) Flack, L. *Acta Crystallogr., Sect. A* **1983**, *39*, 876. (c) Johnson, C. K. *ORTEP—A Fortran Thermal Ellipsoid Plot Program*; Technical Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976. (d) Larson, A. C. *Crystallographic Computing*; Munksgaard: Copenhagen, 1970, 293. (e) Page, Y. L. *J. Appl. Crystallogr.* **1988**, *21*, 983. (f) Page, Y. L.; Gabe, E. J. *J. Appl. Crystallogr.* **1979**, *12*, 464. (g) Rogers, D. *Acta Crystallogr., Sect. A* **1981**, *37*, 7.

(15) Spangenberg, S. F.; Sisler, H. H. *Inorg. Chem.* **1969**, *8*, 1004.

Table 2. ^{31}P NMR Spectroscopic Data for Bis(phosphanyl)hydrazines and Their Metal Complexes

compound	$\delta(^{31}P)$
$Cl_2PN(Me)N(Me)PCl_2$ (**1**)	160.2
$(MeO)_2PN(Me)N(Me)P(OMe)_2$ (**2**)	148.5
$(EtO)_2PN(Me)N(Me)P(OEt)_2$ (**3**)	139.9
$(CF_3CH_2O)_2PN(Me)N(Me)P(OCH_2CF_3)_2$ (**4**)	147.3
$(CH_2{=}CHCH_2O)_2PN(Me)N(Me)P(OCH_2CH{=}CH_2)_2$ (**5**)	142.3
$(CH_3(CH_2)_7O)_2PN(Me)N(Me)P(O(CH_2)_7CH_3)_2$ (**6**)	143.1
$(Pr^iO)_2PN(Me)N(Me)P(OPr^i)_2$ (**7**)	143.0
$(p\text{-}BrC_6H_4O)_2PN(Me)N(Me)P(OC_6H_4Br\text{-}p)_2$ (**8**)	138.0
$(PhO)_2PN(Me)N(Me)P(OPh)_2$ (**9**)	137.0
$(CH_2{=}CHCH_2C_6H_4O\text{-}o)_2PN(Me)N(Me)P(o\text{-}OC_6H_4CH_2CH{=}CH_2)_2$ (**10**)	137.1
cis-$[Mo(CO)_4\{(CF_3CH_2O)_2PN(Me)N(Me)P(OCH_2CF_3)_2\}]$ (**12**)	194.0
cis-$[Mo(CO)_4\{(PhO)_2PN(Me)N(Me)P(OPh)_2\}]$ (**13**)	172.6
cis-$[W(CO)_4\{(CF_3CH_2O)_2PN(Me)N(Me)P(OCH_2CF_3)_2\}]$ (**14**)	173.9
cis-$[W(CO)_4\{(PhO)_2PN(Me)N(Me)P(OPh)_2\}]$ (**15**)	169.3
cis-$[PdCl_2\{(CF_3CH_2O)_2PN(Me)N(Me)P(OCH_2CF_3)_2\}]$ (**16**)	126.4
cis-$[PdCl_2\{(Pr^iO)_2PN(Me)N(Me)P(OPr^i)_2\}]$ (**17**)	120.7
cis-$[PdCl_2\{(PhO)_2PN(Me)N(Me)P(OPh)_2\}]$ (**18**)	119.3
cis-$[PdCl_2\{(p\text{-}BrC_6H_4O)_2PN(Me)N(Me)P(OC_6H_4Br\text{-}p)_2\}]$ (**19**)	118.4
cis-$[PdCl_2\{(CH_2{=}CHCH_2C_6H_4O\text{-}o)_2PN(Me)N(Me)P(o\text{-}OC_6H_4CH_2CH{=}CH_2)_2\}]$ (**20**)	104.1
cis-$[PtCl_2\{(CF_3CH_2O)_2PN(Me)N(Me)P(OCH_2CF_3)_2\}]$ (**21**)	103.6
cis-$[PtCl_2\{(Pr^iO)_2PN(Me)N(Me)P(OPr^i)_2\}]$ (**22**)	94.8
cis-$[PtCl_2\{(CH_3(CH_2)_7O)_2PN(Me)N(Me)P(O(CH_2)_7CH_3)_2\}]$ (**23**)	99.7
cis-$[PtCl_2\{(p\text{-}BrC_6H_4O)_2PN(Me)N(Me)P(OC_6H_4Br\text{-}p)_2\}]$ (**24**)	95.4

Scheme 1



Scheme 2

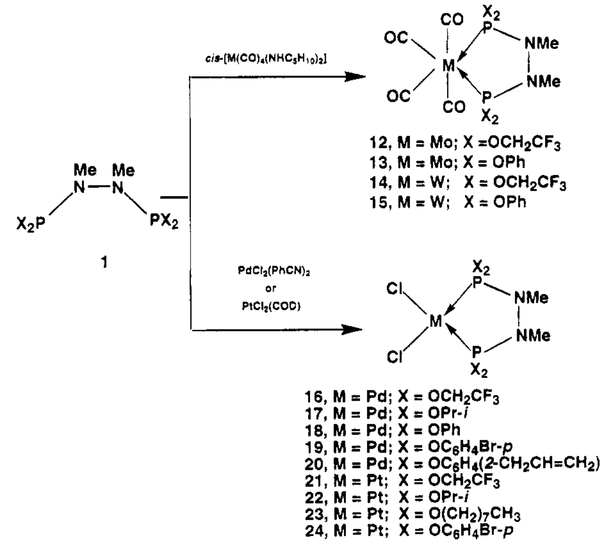


Table 3. Selected Bond Lengths (Å) and Angles (deg) for Compound **15**

W−P1	2.433(2)	W−P2	2.409(2)
W−C1	2.036(6)	W−C2	2.019(6)
W−C3	2.052(2)	W−C4	2.007(6)
P1−N1	1.681(4)	P2−N2	1.715(4)
N1−N2	1.440(6)	C1−O1	1.128(8)
C2−O2	1.140(8)	C3−O3	1.125(7)
C4−O4	1.143(8)		
P1−W−P2	75.9(6)	P1−W−C1	90.0(2)
P1−W−C2	172.5(2)	P1−W−C3	95.7(1)
P1−W−C4	93.4(2)	P2−W−C1	90.2(9)
P2−W−C2	98.4(2)	P2−W−C3	89.9(2)
P2−W−C4	169.0(2)	C1−W−C2	85.2(2)
C1−W−C3	174.4(2)	C1−W−C4	88.6(2)
C2−W−C3	89.2(2)	C2−W−C4	92.5(2)
C3−W−C4	88.6(2)	W−C1−O1	178.1(5)
W−C2−O2	176.8(5)	W−C3−O3	174.4(4)
W−C4−O4	177.1(6)	W−P1−N1	109.2(2)
W−P2−N2	110.8(1)	P1−N1−N2	117.3(3)
P2−N2−N1	105.2(3)		

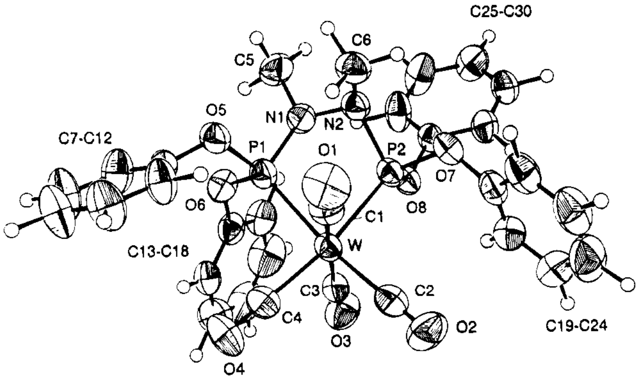


Figure 1. ORTEP drawing of **15** showing 50% probability ellipsoids.

small coupling constants of 2.4−3.0 Hz may be due to the virtual coupling with the two phosphorus centers. The X-ray structural analysis of **15** has been undertaken as a representative example. The ORTEP plot shown in Figure 1 confirms that the structure of **15** comprises the neutral monomeric five-membered chelate of W(0). The five-membered ring is nonplanar with N(2) deviating from the plane of the W(0) metallacycle by 0.65 Å in an envelope fashion. Selected bond distances and angles for **15** are summarized in Table 3. The complex shown in Figure 1 contains W(0) in a distorted octahedral geometry with the bisphosphane, $(PhO)_2PN(Me)N(Me)P(OPh)_2$, chelating in a *cis* fashion via the two phosphorus centers. The *cis* disposition of the carbonyl groups as indicated by the IR spectrum of **15** is seen in its structure. The metal carbonyl distances W−C2 (2.019(6) Å) and W−C4 (2.007(6) Å) are shorter compared to W−C1 (2.036(6) Å) and W−C4 (2.052(2) Å). In addition, the

C−O distances corresponding to the W−C2 (C2−O2 = 1.140(8) Å) and W−C4 (1.143(8) Å) groups are longer compared to the C−O distances of the W−C1 (C1−O1 = 1.128(8) Å) and W−C3 (C3−O3 = 1.125(7) Å) carbonyls. The carbonyl groups C2−O2 and C4−O4 are *trans* to the P1 and P2 phosphorus centers, respectively. The C1−O1 and C3−O3 groups are disposed *trans* to each other across the metal center. Interestingly, the geometry around both N1 (ΣN1 = 354.3) and N2 (ΣN2 = 337.0) is trigonal pyramidal. The longer P−N distances in **15**, compared to the Pd(II) analogue **19**, (P1−N1 = 1.681(4) Å and P2−N2 = 1.715(4) Å in **15**) can be explained based on somewhat weaker nitrogen−phosphorus pπ−dπ interaction (*vide infra*).

The interaction of alkoxy- and aryloxy-functionalized bis(phosphanyl)hydrazines with $Pd(PhCN)_2Cl_2$ in dichloromethane resulted in the formation of *cis*-$[PdCl_2\{(RO)_2PN(Me)N(Me)P(OR)_2\}]$ (R = CH_2CF_3 (**16**), *i*-Pr (**17**), Ph (**18**), C_6H_4Br-*p* (**19**) $C_6H_4(2\text{-}CH_2CH{=}CH_2)$ (**20**)) (Scheme 2). The corresponding reactions with $Pt(COD)Cl_2$ resulted in the formation of *cis*-$[PtCl_2\{(RO)_2PN(Me)N(Me)P(OR)_2\}]$ (R = CH_2CF_3 (**21**), *i*-Pr (**22**), $(CH_2)_7CH_3$ (**23**) C_6H_4Br-*p* (**24**) (Scheme 2). The structures of all the complexes have been established by combination of spectroscopic and elemental analysis. The ^{31}P NMR spectra of all the palladium complexes **16−24** show single resonances owing to the presence of both phosphorus nuclei in similar chemical environments. The chemical shifts of all the Pd(II) complexes (**16−20**) appear in the range of 104−127 ppm whereas those of Pt(II) complexes (**21−24**) show resonances in the range 80−105 ppm. The large $^1J_{PtP}$ coupling value (~5400 Hz) is attributed to *cis* configuration around the platinum center and the value is very large compared to the values observed for other phosphine complexes reported in the literature.[16] This clearly demonstrates the strong platinum−phosphorus interactions as complemented by shorter Pt−P bond distances.[6] The ^1H NMR spectra for all the complexes is consistent with the proposed structures. The NCH_3 resonances for all the Pd(II) and Pt(II) complexes appear in the range 2.75−2.95 ppm as triplets for the Pt(II) complex **21** in which it appears as a doublet of doublets. The coupling constants ($^3J_{PH} + {}^4J_{PH}$) of all the Pd(II) and Pt(II) complexes are in the range of 4.8−5.2 and 2.9−5.0 Hz, respectively. In general, the P−H coupling values of both Pd(II) and Pt(II) complexes (**16−24**) are larger compared to Mo(0) and W(0) complexes (**12−15**), which in turn are larger than the free-ligand values (**2−8**).

The X-ray crystal structure analysis of a representative Pd(II) complex **19** has been carried out. An ORTEP diagram of the structure **19** is shown in Figure 2 and the selected bond distances and angles are listed in Table 4. There are two neutral monomeric molecules in the unit cell with no unusual intermolecular contacts. The complex, shown in Figure 2, contains Pd in a typical square planar environment with the two phosphine units of the bis(phosphanyl)hydrazine coordinated in a *cis* fashion. The geometry around both the nitrogen centers N1 and N2 in **19** is trigonal planar with the angles adding to ~360°. It is interesting to note that the P−N bonds in the palladium complex **19** are shorter compared to those in the tungsten complex **15** (Tables 3 and 4). On the basis of the electronic characteristics of CO (π-acid) and Cl (π-base), bonded to W(0) and Pd(II) in *trans* fashion respectively, one would expect shorter P−N bonds for the tungsten complex **15** as compared to the palladium complex **19**. The observed reversal in the P−N bond distances of **15** and **19** may be explained in terms of the ring confirmations. The five-membered ring in **15** is effectively planar, suggesting efficient Pd−P interaction. Therefore, the shortening of the P−N bonds in **19** may be a consequence of the localization of electronic charge across the Pd−P−N segment of the near-planar ring. Our previous studies on the X-ray crystal structures of Pt(II) complexes of similar bis(phosphanyl)hydrazines also support such a bonding description for the P−N bond distances.[9] On the other hand, the five-membered ring in W(0) complex is nonplanar with N(2) deviating from the five-membered plane by 0.65 Å. The nonplanarity of the five-membered ring coupled with the trigonal pyramidal geometry around N2 (ΣN2 = 337°; ΣN1 = 354°) may lead to poor overlap of the appropriate π-orbitals of the nitrogen centers with the d-orbitals of phosphorus in **15**. This is reflected by longer P−N distances in **15** compared to those in **19**.

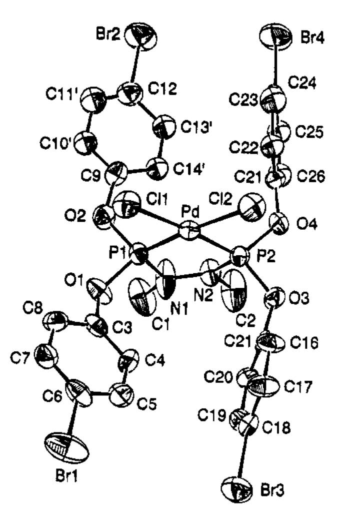


Figure 2. ORTEP drawing of **19** showing 50% probability ellipsoids.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for Compound **19**

Pd−P1	2.175(5)	Pd−P2	2.187(5)
Pd−Cl1	2.346(5)	Pd−Cl2	2.331(5)
P1−N1	1.649(17)	P2−N2	1.652(14)
N1−N2	1.389(22)	N1−C1	1.44(3)
N2−C2	1.49(3)		
Cl1−Pd−Cl2	96.0(2)	Cl1−Pd−P1	175.7(2)
Cl2−Pd−P2	89.9(2)	Cl2−Pd−P1	88.3(2)
Cl2−Pd−P2	175.2(2)	P1−Pd−P2	85.8(2)
Pd−P1−N1	108.4(6)	Pd−P2−N2	107.5(5)
P1−N1−N2	117.3(12)	P2−N2−N1	118.3(11)

The Nature of N−N Bonds and the Oxidative Stability of (Phosphanyl)hydrazines. The N−N bonds in the bis(phosphanyl)hydrazines **2−10** are stable in common organic solvents including in boiling toluene. The N−N bonds in these compounds may be considered as hybrid hydrazines because they are stable to atmospheric hydrolysis (~24 h). It may be noted that the simple hydrazines (e.g. *N*-methylhydrazine or free hydrazine) tend to show marked thermal and hydrolytic instabilities. We have evaluated the oxidative stability of the trifluoroethoxy (**4**) and phenoxy (**9**) derivatives using ^{31}P NMR spectroscopy. Upon exposure to the atmospheric moisture **4** and **9** showed less than 5% conversion to the corresponding phosphine oxides in 12 h. In fact, ~10% conversion to the corresponding phosphine oxides were noted when **4** and **9** were stored in solutions of ethanol−water (1:1 v/v, 12 h). In addition, examinations of the products from the reaction of bisphosphanyl hydrazides **2−10** with various transition metal precursors also indicated the absence of any species resulting from the cleavage of N−N bonds. These observations suggest kinetic and

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(16) (a) Nixon, J. F.; Pidcock, A. *Annu. Rev. NMR Spectrosc.* **1969**, *2*, 345 and references therein; (b) McCrindle, R.; McAlees, A. J. *Organometallics* **1993**, *12*, 2445.

thermodynamic inertness of N–N bonds in **2–10** toward reactions with the early and late transition metal precursors. The hydrolytic/thermal stability of N–N bonds and the oxidative stability of the P^{III} center(s), in bis(phosphanyl)hydrazines present attractive potential in their utility as general purpose bis(phosphines) for use in coordination chemistry.

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Supporting Information Available: Tables of experimental details, bond distances and angles, H atom coordinates, and thermal parameters for **6** (11 pages). Ordering information is given on any current masthead page.

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