Inorg. Chem. **1994**, *33*, 2695–2696 **2695**

Transition Metal Chemistry of Main Group Hydrazides. 7.[†] Synthesis and Coordination Chemistry of Bis(dichlorophosphino)dimethylhydrazine

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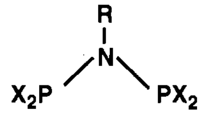
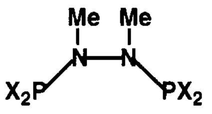
Received December 3, 1993

Introduction

Since the discovery of bis(dihalophosphino)amines[1–3] (**A**), extensive research has been carried out on the main group and transition metal/organometallic chemistry of this class of ligand systems.[1–15] In sharp contrast, the corresponding studies of the dinitrogen-bridged diphosphines, bis(dihalophosphino)dimethylhydrazine (**B**), are surprisingly limited to a few reports.[16–18]



A



B

This may be, in part, due to the lack of a rational synthetic route for such ligands. Gilje et al. and Nöth et al. have pioneered the synthesis of hydrazido phosphines of the type **B**; however, their synthetic strategies involved (i) the condensation of PCl_3 with the highly unstable 1,2-dimethylhydrazine at −196 °C[16,17] and (ii) the treatment of the heterocyclic-cage compound $P[N(Me)N(Me)]_3P$ with PCl_3.[18] Aside from giving low yields of $Cl_2PN(Me)N(Me)PCl_2$ (15–20%), these methods suffer from practical disadvantages, as mentioned above. Therefore, the development of a one-step, straightforward, and high-yield synthetic route to $Cl_2PN(Me)N(Me)PCl_2$ may have significant advantages in the long-term use of this ligand and its derivatives in the coordination chemistry of transition metals. In continuation of our studies on the transition metal chemistry of main group hydrazides,[19–25] we report herein a novel synthetic route to $Cl_2PN(Me)N(Me)PCl_2$ (**1**). The coordination chemistry of **1** with the Pt(II) and Pd(II) precursors is also described.

Experimental Section

All reactions were carried out under an atmosphere of pure nitrogen by using standard Schlenk-line techniques. Solvents were purified, dried, and distilled under nitrogen prior to use. ^{1}H and ^{31}P NMR spectra were recorded on Bruker AMX-500 instrument using $CDCl_3$ solvent. ^{1}H NMR chemical shifts are reported in ppm, downfield from external standard $SiMe_4$. The ^{31}P NMR spectrum was recorded with 85% H_3PO_4 as an external standard. Elemental analyses were performed by Oneida Research Services, Inc., New York. Reagents such as 1,2-dimethylhydrazine dihydrochloride, PCl_3, $PdCl_2(PhCN)_2$, and $PtCl_2(COD)$ were purchased from Aldrich Chemical Co. and were used without further purification. 1,2-Dimethylhydrazine dihydrochloride was dried in vacuo for 4–5 h at 80 °C prior to use.

Synthesis of $Cl_2PN(Me)N(Me)PCl_2$ (1). Phosphorus trichloride (100 g, 0.728 mol) was added dropwise to a finely crushed sample of 1,2-dimethylhydrazine dihydrochloride (10 g, 0.075 mol) at 25 °C. The reaction mixture was heated under reflux till the solution became clear (36 h). The excess of PCl_3 was removed in vacuo after filtration, to obtain compound **1** in 92% yield, as a colorless viscous oil. Anal. Calcd for $C_2H_6Cl_4N_2P_2$: C, 9.2; H, 2.3; N, 10.8; Cl, 53.8. Found: C, 9.4; H, 2.4; N, 10.6; Cl, 54.5. ^{1}H NMR: δ 3.15 (t, ^3J(P–H) = 3.7 Hz, NCH_3). ^{31}P NMR: δ 160.2 (s).

Synthesis of *cis*-$[PdCl_2\{Cl_2PN(Me)N(Me)PCl_2\}]$ (2). A dichloromethane (20 mL) solution of **1** (0.21 g, 0.790 mmol) was added dropwise at 25 °C to a solution of $PdCl_2(PhCN)_2$ (0.30 g, 0.785 mmol) also in dichloromethane (25 mL). The reaction mixture was stirred for 30 min before the solvent was removed in vacuo to obtain a yellow microcrystalline powder. This was washed with hexane to remove the benzonitrile and dried in vacuo to afford complex **2** in 95% yield. Mp: >250 °C. Anal. Calcd for $C_2H_6Cl_6N_2P_2Pd$: C, 5.5; H, 1.4; N, 6.4; Cl, 48.2. Found: C, 5.6; H, 1.5; N, 6.3; Cl, 48.7. ^{1}H NMR: δ 3.28 (t, ^3J(P–H) + ^4J(P–H) = 7.0 Hz, NCH_3). ^{31}P NMR: δ 151.9(s).

Synthesis of *cis*-$[PtCl_2\{Cl_2PN(Me)N(Me)PCl_2\}]$ (3). A dichloromethane (20 mL) solution of **1** (0.215 g, 0.825 mmol) was added dropwise at 25 °C to a solution of $PtCl_2(COD)$ (0.30 g, 0.806 mmol) also in dichloromethane (25 mL). The reaction mixture was stirred for 2 h and worked up as described for **2** to obtain a colorless microcrystalline powder of **3** in 90% yield. Mp: 180 °C. Anal. Calcd for $C_2H_6Cl_6N_2P_2Pt$: C, 4.6; H, 1.2; N, 5.3; Cl, 40.0. Found: C, 4.6; H, 1.4; N, 5.5; Cl, 40.4. ^{1}H NMR: δ 3.25 (t, ^3J(P–H) + ^4J(P–H) = 7.0 Hz, NCH_3). ^{31}P NMR: δ 121.4 (s, ^1J(Pt–P) = 5196 Hz).

Results and Discussion

The new synthetic route to produce bis(dichlorophosphino)dimethylhydrazine (**1**) involved the treatment of PCl_3 with 1,2-dimethylhydrazine dihydrochloride (eq 1). Phosphorus trichloride

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[†] Part 6 is ref 24.

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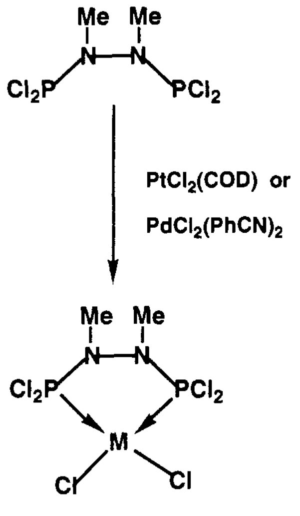
Scheme 1



M = Pd, **2**; Pt, **3**

was used as both solvent and reactant, and the mixture was refluxed for 36 h to obtain $Cl_2PN(Me)N(Me)PCl_2$ (**1**) in 92%

$$\mathrm{HMeNNHMe{\cdot}2HCl + excess\ PCl_3 \rightarrow \underset{\mathbf{1}}{Cl_2PN(Me)N(Me)PCl_2} + 4HCl} \quad (1)$$

yield. The ^{31}P NMR spectrum of the product consisted of a single peak at 160.2 ppm. The ^{1}H NMR spectrum of **1** consisted of a deceptively simple triplet centered at 3.15 ppm (^{3}J(P–H) = 3.7 Hz), presumably, due to virtual coupling. The high yield and the purity of **1** remained unchanged even when the above reaction was carried out in 50–100-g scales, suggesting the feasibility of this reaction in large scales.

The presence of two trivalent phosphorus centers in **1** presents the possibility of using it as a π-acid donor toward transition metals. For example, **1** reacted smoothly with $PdCl_2(PhCN)_2$ and $PtCl_2(COD)$ to produce the new metallacyclic compounds $[Cl_2PN(Me)N(Me)PCl_2MCl_2]$ (M = Pd (**2**), Pt (**3**)) containing Pd(II) and Pt(II) centers, respectively (Scheme 1). The chemical compositions of **2** and **3** were confirmed by C, H, N, and Cl analytical data. The solution molecular weight analyses of **2** and **3** indicated them to be monomeric in solution.

The ^{31}P NMR spectra of **2** and **3** (Figure 1) in $CDCl_3$ revealed sharp singlet signals at 151.9 and 121.4 ppm (^{1}J(Pt–P) = 5196 Hz), respectively. The upfield (more negative) ^{31}P chemical shifts on going from the free ligand **1** (160.2 ppm) to the Pd(II), **2**, (151.9 ppm), and Pt(II), **3** (121.4 ppm), complexes have been noted earlier for a number of Pd(II)/Pt(II) complexes of $R_2PNR'PR_2$ and cyclic P_2N_2 ligand systems.[4–15] However, a considerable upfield ^{31}P chemical shift on going from **2** to **3** ($\delta_{^{31}P}(\mathbf{2}) - \delta_{^{31}P}(\mathbf{3}) = 30.5$ ppm) may be rationalized in terms of somewhat stronger M–P bonding interaction in the platinum complex than in the palladium complex. The large ^{1}J(Pt–P) value (Figure 1) suggests that complex **3** contains Pt(II) presumably in a square-planar environment with the P–N–N–P unit chelating in a cis fashion via the two phosphine units.[4a] The large ^{1}J(Pt–P) value also suggests that both the phosphine groups in **3** are trans to the polarizable chloride substituents in **3**.[26,27]

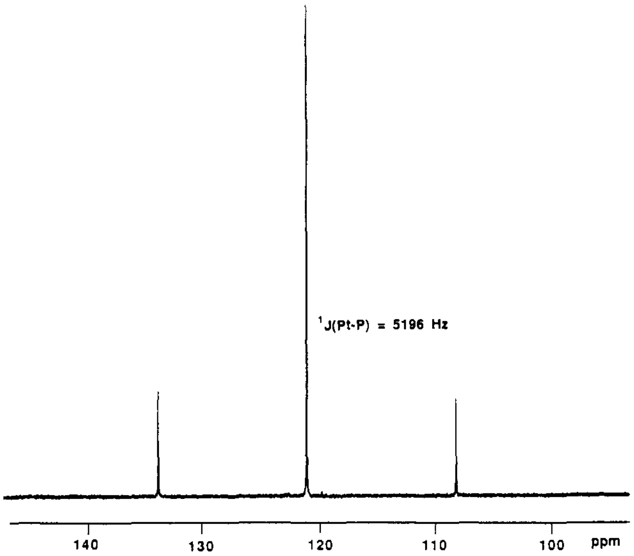


Figure 1. $^{31}P\{^{1}H\}$ NMR (202.5 MHz) spectrum of *cis*-$[PtCl_2\{Cl_2PN(Me)N(Me)PCl_2\}]$ (**3**) in $CDCl_3$ showing the ^{195}Pt satellites.

Conclusions

It has been noted that the reactions of bis(dichlorophosphino)-amines, $Cl_2PN(R)PCl_2$, with transition metal precursors generally produce complex reaction products. In fact, the coordination chemistry of $RPCl_2$ type of ligands is mostly limited to the formation of metal phosphonium salts.[3–15,28] In sharp contrast, the formation of **2** and **3** in nearly quantitative yields starting from $Cl_2PN(Me)N(Me)PCl_2$ in unique. Assuming that the P–Cl bonds in **2** and **3** retain their reactivity toward nucleophilic substitution reactions, the reactions at the phosphorus centers in **2** and **3** should provide new opportunities in the development of an extensive chemistry of the coordinated ligand systems. Our efforts are presently underway along these lines.

Acknowledgment. This work was supported by funds provided by DOE Grant DEFG0289ER60875 and by the Departments of Chemistry, Radiology, and Research Reactor, University of Missouri.

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