Transition Metal Chemistry of Main Group Hydrazides, 9[1c]

Platinum Complexes of Diphosphanylhydrazides $R_2PN(Me)N(Me)PR_2 \cdot PtCl_2$ ($R = OPh$, o-$OC_6H_4CH_2CHCH_2$)

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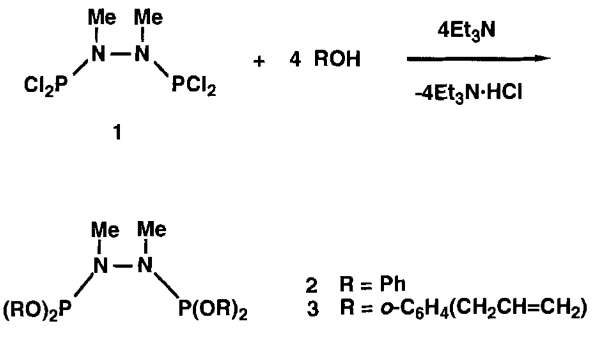
While the transition metal complexes of bis(phosphanyl)amines ($P^{III}-N-P^{III}$) have been known for over three decades, the ligating properties of the next homologue $P^{III}-N-N-P^{III}$ have been unprecedented so far. The X-ray structures of cycloplatinaphosphanehydrazides, $[(OR)_2PN(Me)N(Me)P(OR)_2$-$PtCl_2]$, reveal short distances for the P−N [1.639(5) Å] bonds.

The coordination chemistry of $R_2PN(R')PR_2$ based ligands is an area of increasing interest owing to the synthetic versatility and structural diversity exhibited by this class of compounds[1−15]. Since the discovery of bis(dihalophosphanyl)amines (**A**), to date, more than 300 papers have been published describing the rich coordination chemistry of $R_2PN(R')PR_2$-type of ligand frameworks[1−15]. These ligands have shown varied bonding modes with the transition metals, which include (a) monodentate ligation through the interaction with P(III); (b) bidentate chelate or bridging coordination and; (c) metal-nitrogen σ-bond formation by means of the reaction at the amino nitrogen center[1]. In contrast, the main group chemistry of the next homologue $R_2PN(R')N(R')PR_2$ ($R = Cl$, Me, NMe_2) (**B**), are surprisingly limited to a few reports[16].

Scheme 1

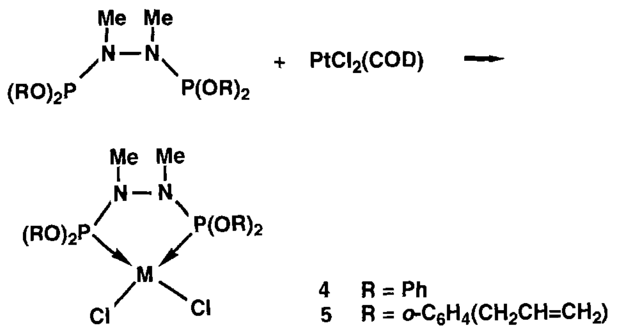


The coordination chemistry of the $R_2PN(R')N(R')PR_2$-based ligands has not yet been developed. $Cl_2PN(Me)N(Me)PCl_2$ (**1**) is now readily available[17] and is an excellent precursor to produce functionalized diphosphanylhydrazides, e.g. $(RO)_2PN(Me)N(Me)P(OR)_2$. The development of the transition metal chemistry of $R_2PN(R')N(R')PR_2$ systems is of particular significance because it would be reminiscent of the coordination chemistry of $R_2P(CH_2)_2PR_2$ ligand frameworks; a class of ligands which have demonstrated significant applications in catalysis. As part of our ongoing studies on the transition metal chemistry of new phosphorus-nitrogen ligating systems[18−25], we report on the coordination chemistry of $(RO)_2PN(R')N(R')P(OR)_2$ compounds.

The aryloxy-functionalized dinitrogen-bridged diphosphanes $(RO)_2PN(Me)N(Me)P(OR)_2$ [$R = C_6H_5$, **2**; o-C_6H_4-$(CH_2CH{=}CH_2)$, **3**] were obtained from the reactions of the corresponding phenols with $Cl_2PN(Me)N(Me)PCl_2$ (**1**) in the presence of Et_3N in about 95% yield (Scheme 1). The new diphosphanes **2** and **3** are air stable viscous liquids. The ^{31}P-NMR spectra of **2** and **3** consisted of single resonances at 138.1 and 138.0 ppm, respectively, indicating a significant shielding as compared to the single nitrogen bridged analogue: $(PhO)_2PN(Me)P(OPh)_2$ ($\delta^{31}P = 143.0$)[26]. The interaction of $PtCl_2(COD)$ with **2** or **3** in dichloromethane resulted in the formation of $[(RO)_2PN(Me)N(Me)P(OR)_2PtCl_2]$ [R = Ph, **4**; o-$C_6H_4(CH_2$-$CH{=}CH_2)$, **5**] in good yields (Scheme 2). These compounds represent first examples of cycloplatina(II)phosphane hydrazides. Confirmative evidence for the structures of **4** and **5** has come from the X-ray crystallographic analysis of their single crystals[27]. The ORTEP plots shown in Figures 1 and 2 respectively, reveal that the structures of **4** and **5** comprise the neutral monomeric complexes. They contain Pt(II) in a typical square-planar environment with the phosphanes chelating *via* a *cis* disposition in a five-membered metallacyclic framework.

The most striking feature in the structures of **4** and **5** concerns the P−N bond lengths. The P−N distances observed for both **4** [P1−N1, 1.639(5) Å and P2−N2, 1.669(5) Å] and **5** [P1−N1, 1.651(8) Å and P2−N2, 1.665(8) Å] are

Scheme 2



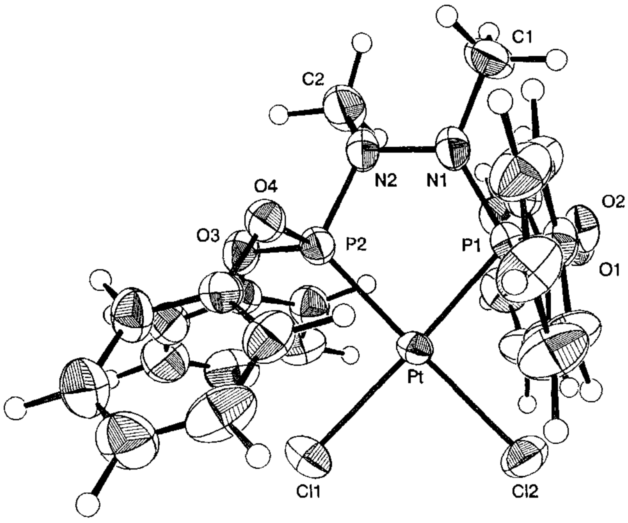


Figure 1. Molecular structure of **4**. – Selected bond distances [Å] and angles [°]: Pt–Cl1 2.329(1), Pt–Cl2 2.354(1), Pt–P1 2.182(1), Pt–P2 2.180(1), P1–N1 1.639(5), P2–N2 1.669(5), N1–N2 1.440(6); Cl1–Pt–Cl2 90.6(1), Cl1–Pt–P1 176.3(1), Cl1–Pt–P2 91.7(1), Cl2–Pt–P2 177.5(1), P1–Pt–P2 84.7(5), P1–N1–N2 119.7(3), P2–N2–N1 110.6(3), Pt–P1–N1 108.0(2), Pt–P2–N2 110.7(2)

much shorter than the value generally accepted for P–N single bonds (1.75–1.80 Å)[1,30], signifying possible P–N multiple bond character. In fact, the length of one of the P–N bonds in **4** [P1–N1, 1.639(5) Å] and **5** [P1–N1, 1.651(8) Å] may be regarded as the shortest P–N single bond known, todate, for the metal complexes of the P^{III}–N class of ligands[1]. For compound **4**, it is interesting to note that the geometries around N1 and N2 are different. The geometry around N1 is trigonal planar, whereas, it is trigonal pyramidal around N2. Therefore, the P1–N1 distance in **4** [1.639(5) Å] is shorter than P2–N2 [1.669(5) Å]. The geometries around N1 and N2 in **5** are trigonal planar and, therefore, the P–N distances in this compound are nearly identical. This significant shortening of the P–N bond length may be a consequence of the localization of electronic charge across the Pt–P–N segment of **4** and **5**. Such a bonding description which would require stronger Pt–P interaction, is also reflected in the short Pt–P bond lengths [average Pt–P = 2.176(1) Å for **4** and 2.177(3) Å for **5**]. The large ^{1}J(Pt–P) values of 5497 and 5537 Hz for **4** and **5**, respectively, would be consistent with the stronger Pt–P interactions in these complexes.

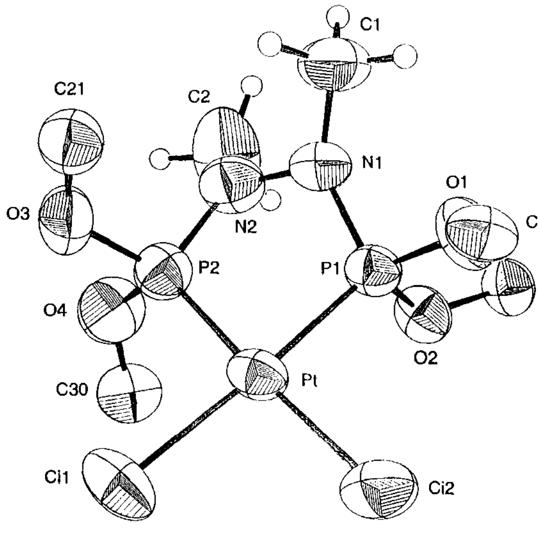


Figure 2. Molecular structure of **5**. The phenyl ring atoms are omitted for clarity. – Selected bond distances [Å] and angles [°]: Pt–Cl1 2.341(3), Pt–Cl2 2.336(3), Pt–P1 2.174(2), Pt–P2 2.181(3), P1–N1 1.651(8), P2–N2 1.665(8), N1–N2 1.415(12); Cl1–Pt–Cl2 92.2(1), Cl1–Pt–P1 176.2(1), Cl1–Pt–P2 92.2(1), Cl2–Pt–P2 175.1(1), P1–Pt–P2 84.0(1), P1–N1–N2 111.4(6), P2–N2–N1 115.2(6), Pt–P1–N1 108.4(3), Pt–P2–N2 108.1(3)

Further studies to uncover the new coordination chemistry of $R_2PN(R')N(R')PR_2$-type of ligands are underway.

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Experimental

All operations were carried out under a nitrogen atmosphere in dry, N_2-saturated solvents. Compound **1** was prepared according to ref.[17]. $PtCl_2(COD)$, C_6H_5OH and o-$HOC_6H_4(CH_2CH=CH_2)$ were purchased from Aldrich Chemical Co. USA.

2: A mixture of phenol (7.02 g, 76.3 mmol) and Et_3N (7.71 g, 76.3 mmol), in *n*-hexane (50 ml) was added dropwise to **1** (5.0 g, 19 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 analytically pure **2** in 90% yield as a viscous liquid. – ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.90 (br., 6H, NCH_3), 7.0–7.3 (m, 20H, C_6H_5). – ^{31}P NMR (202.5 Hz, $CDCl_3$): δ = 138.1 (s). – $C_{26}H_{26}N_2O_4P_2$ (492.1): calcd. C 63.40, H 5.32, N 5.69; found C 63.03, H 5.67, N 6.12.

3: Compound **3** was obtained in 85% yield by using 2-allylphenol in the procedure as described above for **2**. – ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.1 (br., 6H, NCH_3), 3.35 (m, br., 8H, $C_6H_4CH_2CH$), 5.0 (m, br., 8H, $CH=CH_2$), 5.90 (m, br., 4H, $CH_2CH=CH_2$), 7.95–7.30 (m, 16H, C_6H_4). – ^{31}P NMR (202.5 MHz, $CDCl_3$): δ = 138.0 (s). – $C_{38}H_{42}N_2O_4P_2$ (652.3): calcd. C 69.91, H 6.49, N 4.29; found C 70.02, H 6.67, N 4.63.

4: A dichloromethane solution of **2** (0.40 g, 0.81 mmol) was added dropwise to a solution of $PtCl_2(COD)$ (0.30 g, 0.81 mmol) also in dichloromethane (25 ml) at 25°C. The reaction mixture was stirred for 2 h before the solvent was removed in vacuo to obtain a white microcrystalline powder. This was washed from hexane to remove the cyclooctadiene, and dried in vacuo to obtain the complex **3** in 95% yield; m.p. 196°C. – ^{1}H NMR (500 MHz, $CDCl_3$):

δ = 2.83 [t, ^3J(P,H) + ^4J(P,H) = 4.4 Hz, 6H, NMe], 7.0−7.5 (m, 20H, Ph). − ^{31}P NMR (202.5 Hz, $CDCl_3$): δ = 95.7 [s, ^1J(Pt,P) = 5497 Hz]. − $C_{26}H_{26}Cl_2N_2O_4P_2Pt$ (757.0): calcd. C 41.21, H 3.46, N 3.70; found C 41.42, H 3.49, N 3.82.

5: Complex **5** was obtained in about 95% by using the ligand **3**, by the procedure as described above for **4**; m.p. 165°C. − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.9 [t, ^3J(P,H) + ^4J(P,H) = 4.4 Hz, NCH_3], 3.4 [*AB*X pattern, $^2J(H_A,H_B)$ = 15.9 Hz, $^3J(H_A,H_X)$ = 6.2 Hz, 8H, $C_6H_4CH_2CH$], 5.0 [*AM*X pattern, $^3J(H_X,H_M)$ = 17.0 Hz, $^3J(H_X,H_A)$ = 10.0 Hz, $^2J(H_A,H_M)$ = 1.5 Hz, 8H, $CH{=}CH_2$], 5.87 (m, 4H, $CH_2CH{=}CH_2$), 7.10−7.30 (m, 16H, C_6H_4). − ^{31}P NMR (202.5 Hz, $CDCl_3$): δ = 80.4 [s, ^1J(Pt,P) = 5536 Hz]. − $C_{36}H_{36}Cl_2N_2O_4P_2Pt$ (917.2): calcd. C 49.72, H 4.62, N 3.05; found C 49.63, H 4.76, N 3.21.

Crystal Structure Analysis of **4**: Single crystals of **4** were obtained by slow evaporation of a $CDCl_3$ solution and measured at 294 K; crystal size: 0.30 × 0.35 × 0.35 mm; monoclinic, space group $P2_1/n$; $Z = 4$; $a = 10.086(2)$, $b = 22.446(2)$, $c = 12.377(2)$ Å, $\beta = 94.95(1)°$; $V = 2791.6(8)$ Å^3; $\rho_{calcd} = 1.805$ g cm^{-3}; μ(Mo-K_α) = 5.41 mm^{-1}; $M = 758.4$. − Absorption corrections were made, the min. and max. transmission factors are 0.732217 and 0.999028. 3860 unique reflections were measured and 3379 with $I > 2\sigma(I)$ were used in the refinement to $R = 0.027$, $R_w = 0.039$. Atomic scattering factors and anomalous dispersion corrections were taken from the International Tables for X-ray Crystallography[28]. The structure was solved by direct methods using NRCVAX program[29]. All the hydrogen atoms were introduced in the last step of the refinement procedure in calculated positions.

Crystal Structure Analysis of **5**: Single crystals with the dimensions 0.16 × 0.32 × 0.37 mm were obtained by slow evaporation of a $CDCl_3$ solution and measured at 294 K; monoclinic, space group $P2_1/c$; $Z = 4$; $a = 12.975(3)$, $b = 18.234(2)$, $c = 16.811(6)$ Å, $\beta = 94.48(2)°$; $V = 3965.1(2)$ Å^3; $\rho_{calcd.} = 1.505$ gcm^{-3}; μ(Mo-K_α) = 3.83 mm^{-1}; $M = 898.5$. Absorption corrections were made, the min. and max. transmission factors are 0.772971 and 0.999101. 5493 unique reflections were measured and 4323 with $I > 2(I)$ were used in the refinement to $R = 0.046$, $R_w = 0.065$. The structure was solved by direct methods[28,29] and completed by successive Fourier difference maps. The allyl side chains of the phenyl rings proved to be rotationally disordered and these atoms were included in the final model with isotropic thermal parameters, as were the atoms C21 to C26 of one of the rings. The remaining non-hydrogen atoms were included in the model with anisotropic thermal parameters. Though it could be located in a difference map in a position giving reasonable geometry, refinement of atom C27 lead to an unrealistic C26−C27 bond length, and this atom was included in the final model at a fixed position. H atoms for the allyl side chains were omitted from the model. All other H atoms were placed at calculated positions.

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[32/94]