Formation of a Novel Delocalised Diphosphazene upon Complexation. The Preparation and X-Ray Structure of $Pd_2Cl_4[(CF_3)_2P{=}N{=}PPh_3]_2$

H. G. Ang,[a] **Y. M. Cai,**[a] **W. L. Kwik**[a] **and Arnold L. Rheingold**[b]

[a] *Department of Chemistry, National University of Singapore, Lower Kent Ridge Road, Singapore 0511, Republic of Singapore*

[b] *Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware 19716, USA*

Reaction of $(CF_3)_2P{-}N{=}PPh_3(L)$ with $PdCl_2$ in dichloromethane gives $Pd_2Cl_4[(CF_3)_2P{=}N{=}PPh_3]_2$, **1** in which L has been shown from spectroscopic and X-ray crystallographic analyses to assume an uncharged non-linear electronic structure $[Ph_3P{=}N{=}P(CF_3)_2]$, where the P–N and N–P bonds are equidistant and the PNP segment is highly delocalised.

The study of cyclo- and poly-phosphazenes as ligands with transition metals has attracted considerable interest.[1–5] However, the coordinating properties of diphosphazene have received little attention. We report here the Pd^{II} complex **1** containing a monodentate diphosphazene ligand.

The ligand $(CF_3)_2P{-}N{=}PPh_3$ was treated with $PdCl_2$ in dichloromethane at 60 °C for 24 h. The solution turned intensely orange, from which an orange powder was obtained. This was recrystallised from 1 : 1 hexane/CH_2Cl_2 whereupon red crystals of $Pd_2Cl_4[(CF_3)_2P{-}N{=}PPh_3]_2$ **1** formed. The composition of **1** was established by elemental analyses (C, H, N) and ^1H, ^{19}F and ^{31}P NMR spectroscopy.†

The molecular structure of **1** was determined by single-crystal X-ray diffraction.‡ As shown in Fig. 1, the structure of **1** comprises the neutral dimeric complex $Pd_2Cl_4L_2$ in which each Pd assumes a typical square planar environment and the ligand L is bonded through the 'trivalent' phosphorus atom P(1) only. The Pd–P distance (2.204 Å) is somewhat shorter than that of a Pd^{II} phosphoranimine complex $HNPPh_2CH_2PPh_2PdCl_2$ **2**[6] in which a phosphoranimine–phosphine chelate is formed. More significantly the two phosphorus–nitrogen bond lengths [P(2)–N(1) 1.559 Å;

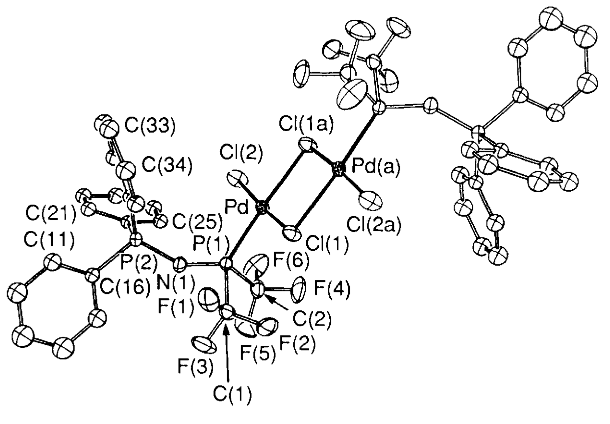

Fig. 1 ORTEP molecular structure and labelling scheme for $[C_{20}H_{15}F_6NPCl_2Pd]_2$. Ellipsoids are at the 30% probability level. Pd · · · Pd(a) 3.481(1), Pd–Cl(1) 2.313(2), Pd–Cl(2) 2.264(3), Pd–P(1) 2.204(2), Pd–Cl(1a) 2.421(2), Pd(a)–Cl(1) 2.421(2), P(1)–N(1) 1.559(6), P(1)–C(1) 1.895(10), P(2)–N(1) 1.583(8), P(1)–C(2) 1.883(12) Å; Cl(1)–Pd–Cl(2) 175.7(1), Cl(1)–Pd–P(1) 98.3(1), Cl(2)–Pd–P(1) 85.9(1), Cl(1)–Pd–Cl(1a) 85.4(1), Cl(2)–Pd–Cl(1a) 90.6(1), P(1)–Pd–Cl(1a) 173.1(1), Pd–Cl(1)–Pd(a) 94.6(1), Pd–P(1)–N(1) 126.8(3), Pd–P(1)–C(1) 114.2(3), N(1)–P(1)–C(1) 103.3(4), Pd–P(1)–C(2) 107.4(3), N(1)–P(1)–C(2) 103.5(4), C(1)–P(1)–C(2) 97.4(5), P(1)–N(1)–P(2) 143.4(5)°.

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† *Selected spectroscopic data* for $Pd_2Cl_4[(CF_3)_2P{-}N{=}PPh_3]$ **1**: ^{19}F NMR (referenced to trifluoroacetic acid) δ 14.0 and 12.9 ppm; ^{31}P NMR (referenced to H_3PO_4) δ_1 44.0 ppm, δ_2 27.60 ppm.

‡ *Crystal data* for **1**: $[C_{20}H_{15}F_6NPCl_2Pd]_2$, triclinic, $P\bar{1}$, $a = 9.238(3)$, $b = 9.926(2)$, $c = 13.694(3)$ Å, $\alpha = 107.336(18)$, $\beta = 93.124(22)$, $\gamma = 103.844(21)°$, $U = 1153.1(5)$ Å^3; $Z = 1$; $D_c = 1.707$ g cm^{-3}; μ(Mo-Kα) = 12.11 cm^{-1}; $T = 23$ °C, Nicolet R3m/μ, Mo-Kα. Of 2603 data ($4 \leqslant 2\theta \leqslant 42°$), 2469 were independent ($R_{int} = 2.20\%$), and 1914 were observed [$5\sigma(F_o)$]. The structure was solved by direct methods. Refinement: all non-hydrogen atoms anisotropic, all hydrogen atoms idealized, phenyl rings constrained as rigid hexagons, $R(F) = 4.30\%$, $R(wF) = 4.65\%$, GOF = 1.166, $N_o/N_v = 11.74$, $\Delta/\sigma = 0.980$, $\Delta/\sigma_{max}) = 0.002$. SHELXTL software used for all computations (G. Sheldrick, Nicolet XRD, Madison, WI, USA). An empirical (psi-scan) correction was performed. The ratio of the transmission coefficients was 1.22. X-Ray data have been deposited at the CCDC. See Notice to Authors.

Scheme 1

P(1)–N(1) 1.583 Å] lie within the range of values for the P–N double bond.[7–10] In particular, the P(1)–N(1) bond is much shorter than would be expected for a P–N single bond (1.75–1.80 Å).

Thus, it would appear that the coordinated ligand $(CF_3)_2P{=}N{-}PPh_3$ assumes a highly delocalised electronic structure over the unsymmetrical P–N–P segment (Scheme 1). This molecular species represents the first example of a delocalised P=N=P non-linear structure.

Such electronic structure is consistent with the observation that the difference in chemical shifts of the P(1) and P(2) atoms is reduced from 30 to 17 ppm in going from free L to the complex **1**. Furthermore, it is of interest to note that the corresponding value reported for **2**[6] was 32 ppm. In the latter the two phosphorus atoms could be distinguished as being trivalent and pentavalent respectively since they are separated by a methylene unit. Interestingly, not only is the average P–N bond distance typical of P=N, also the P–N–P bond angle of 143.4(5)° in **1** falls into the reported range of values for the bis(triphenylphosphine)iminum cation (PPN). For instance, the P=N bonds and the PNP angle are 1.566(7)/1.583(7) Å and 140.9 (5)° respectively for $[PPN][HFe_2(CO)_8]$,[10] and 1.571(5)/1.553(2) Å and 154.8(4)° respectively for $[PPN][Cr_2(CO)_{10}(\mu\text{-}H)]$.[11]

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