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COMMUNICATION

SYNTHESIS AND X-RAY CRYSTAL STRUCTURE OF $(\textit{cis}\text{-}\mathrm{PdCl_2})_2[(\mathrm{Ph_2PNH})(\mathrm{NH})\mathrm{CC_6H_4C}(\mathrm{NH})(\mathrm{NHPPh_2})]\cdot 6\mathrm{DMF}$

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Abstract—The interaction of 1,4-phenylenebis[*N*-(diphenylphosphino-*N*′,*N*′-bis(trimethylsilyl)amidine], $(\mathrm{Ph_2PN})[\mathrm{N(SiMe_3)_2}]\mathrm{C{-}C_6H_4{-}C}[\mathrm{N(SiMe_3)_2}](\mathrm{PPh_2})$, with 2 equivalents of $\mathrm{PdCl_2(PhCN)_2}$ in THF gives $(\textit{cis}\text{-}\mathrm{PdCl_2})_2[(\mathrm{Ph_2PNH})(\mathrm{NH})\mathrm{CC_6H_4C}(\mathrm{NH})(\mathrm{NHPPh_2})]$ in moderate yield. The compound has C_2 symmetry and has been fully characterized by analytical, spectroscopic and X-ray diffraction methods.

Chalcogen-nitrogen heterocycles are π-electron-rich compounds possessing unusual intrinsic molecular and electronic properties and are good candidates for low-dimensional conducting materials.[1] This has led to a considerable interest in the synthesis and reactivity of chalcogen-nitrogen heterocycles in recent years.[2] There is growing interest in the coordination chemistry of these chalcogen-nitrogen heterocycles toward transition metals.[3,4] In this communication, we report the result of the reaction of $\mathrm{PdCl_2(PhCN)_2}$ with 1,4-phenylenebis[*N*-(diphenylphosphino-*N*′,*N*′-bis(trimethylsilyl) amidine], $(\mathrm{Ph_2PN})[\mathrm{N(SiMe_3)_2}]\mathrm{C{-}C_6H_4{-}C}[\mathrm{N(SiMe_3)_2}](\mathrm{NPPh_2})$.

When $(\mathrm{Ph_2PN})[\mathrm{N(SiMe_3)_2}]\mathrm{CC_6H_4C}[\mathrm{N(SiMe_3)_2}](\mathrm{NPPh_2})$ and $\mathrm{PdCl_2(PhCN)_2}$ were allowed to react in a 1 : 2 molar ratio in THF for 2 days at room temperature, work-up gave yellow crystals of stoichiometry $(\mathrm{PdCl_2})_2(\mathrm{C_{32}H_{28}N_4P_2})\cdot 6\mathrm{DMF}$, **I**,† in moderate yield (50%) after recrystallization from a DMF solution. The structure of **I** was established by X-ray diffraction analysis. Crystals of stoichiometry $(\mathrm{PdCl_2})_2[(\mathrm{Ph_2PNH})(\mathrm{NH})\mathrm{CC_6H_4C}(\mathrm{NH}$

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† $(\mathrm{C_{32}H_{28}N_4P_2Cl_4Pd_2})\cdot 6\mathrm{C_3H_7NO}$: yellow crystals, m.p. 302–305°C. Found: C, 45.5; H, 5.4; N, 10.7; Cl, 10.5. Calc. for $\mathrm{C_{50}H_{70}N_{10}O_6Cl_4P_2Pd_2}$: C, 45.4; H, 5.3; N, 10.6; Cl, 10.7%. IR ($\mathrm{cm^{-1}}$, in KBr): 3524w, 3060w, 1640vs, 1582s, 1524m, 1460s, 1432s, 1412m, 1386s, 1354s, 1254m, 1156w, 1100s, 1014w, 878w, 852w, 804s, 746m, 714w, 684s, 664m, 536m, 470m. $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (d_6-DMSO): δ85.3(s) ppm. $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (d_6-DMSO): phenyl and phenylene carbons, δ 133.0, 132.8, 132.6, 129.2, 129.0, 128.8 ppm; DMF carbons, 162.3, 35.7 and 30.7 ppm. ^{1}H NMR (d_6-DMSO): phenyl and phenylene protons, δ 7.60–7.97 (24 H, m) ppm; PdNH protons, δ 10.43 (2H, br s) ppm; PNH protons, δ 9.16 (2H, br s) ppm; DMF protons: CHO protons, δ7.94 (6H, s) ppm; methyl protons, δ 2.68 (18H, s) and 2.72 (18H, s) ppm.

$(NHPPh_2)] \cdot 6DMF$‡ suitable for X-ray diffraction were grown from a solution of DMF. A perspective drawing of **I** is shown in Fig. 1 with selected bond lengths and bond angles given in its caption. The dimeric species is C_2 symmetric and the $(Ph_2PNH)(NH)CC_6H_4C(NH)(NHPPh_2)$ ligand acts as a bridging bidentate ligand with the imino group N(2) and the phosphino group P(1) coordinated to each of the two $PdCl_2$ moieties forming two five-membered rings. The geometry of the palladium(II) centres are approximately square planar with the two chloro ligands adopting a *cis* configuration.

Within the ligand, the P(1)—N(1) bond length of 1.704(7) Å is in the normal range for a phosphorus–nitrogen single bond. The C(1)—N(1) and C(1)—N(2) distances of 1.359(10) and 1.298(10) Å, respectively, are intermediate between those expected for single (1.46 Å) and double (1.25 Å) bonds indicating some delocalization about the N—C—N framework. The delocalization is also reflected in the P(1)—N(1)—C(1) bond angle of 117.0(6)°, a significant deviation from the expected for a tetrahedral sp^3 nitrogen atom. Similar observation has been reported for related platinum and rhodium complexes.[5]

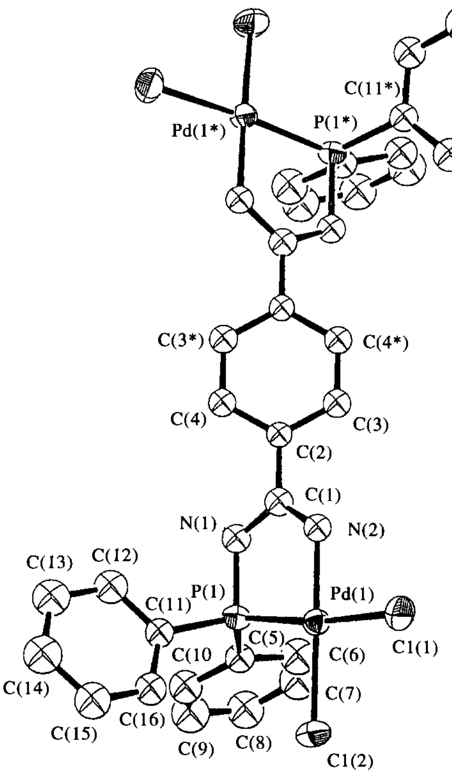

Fig. 1. A perspective view of the molecular structure of $(cis\text{-}PdCl_2)_2[(Ph_2PNH)(NH)CC_6H_4C(NH)(NHPPh_2)]$. Selected bond lengths (Å) and bond angles (°): Pd(1)—Cl(1), 2.359(3); Pd(1)—Cl(2), 2.314(2); Pd(1)—P(1), 2.194(2); Pd(1)—N(2), 2.018(6); P(1)—N(1), 1.704(7); N(1)—C(1), 1.359(10); N(2)—C(1), 1.298(10); Cl(1)—Pd(1)—Cl(2), 94.39(9); Cl(1)—Pd(1)—N(2), 90.4(2); Cl(2)—Pd(1)—P(1), 92.61(9); P(1)—Pd(1)—N(2), 82.8(2); P(1)—N(1)—C(1), 117.0(6); N(1)—C(1)—N(2), 118.9(7); Pd(1)—N(2)—C(1), 120.(5).

The spectroscopic data of **I** are consistent with its solid state structure. The $^{31}P\{^1H\}$ NMR spectrum of **I** in d_6-DMSO exhibited a singlet at δ 85.3 ppm for the two PPh_2 groups. This suggests that the two PPh_2 groups had identical environments. The positive increase in the chemical shift for the PPh_2 groups (from δ 34.5 to 85.3 ppm) is characteristic of chelate ring formation.[6] In addition to the resonances expected for the phenyl and phenylene protons, the ^1H NMR spectrum of **I** exhibited two broad singlets at δ 10.43 (integral 2 H) and 9.16 ppm (integral 2 H). These resonances are due to the different NH groups in the five-membered ring. Based on the chemical shifts of related compounds,[5] the resonances at δ 9.16 and 10.43 ppm can be assigned to the proton of the NH group next to the phosphorus and the NH group coordinated to palladium respectively. Resonances corresponding to the $SiMe_3$ groups were not observed in either ^1H or ^{13}C NMR spectra. The IR spectrum of the complex in KBr exhibited a broad band at 3524 cm^{-1} which further supported the presence of the NH groups. In all the spectra, absorptions due to the solvent of recrystallization, DMF, were observed.

A possible mechanism for the formation of **I** is shown in Scheme 1. The ligand reacted with 2 equivalents of $PdCl_2(PhCN)_2$ to produce intermediate **II**, which underwent rapid 1,3-silyl shift to give intermediate **III**. **III** was then hydrolysed to

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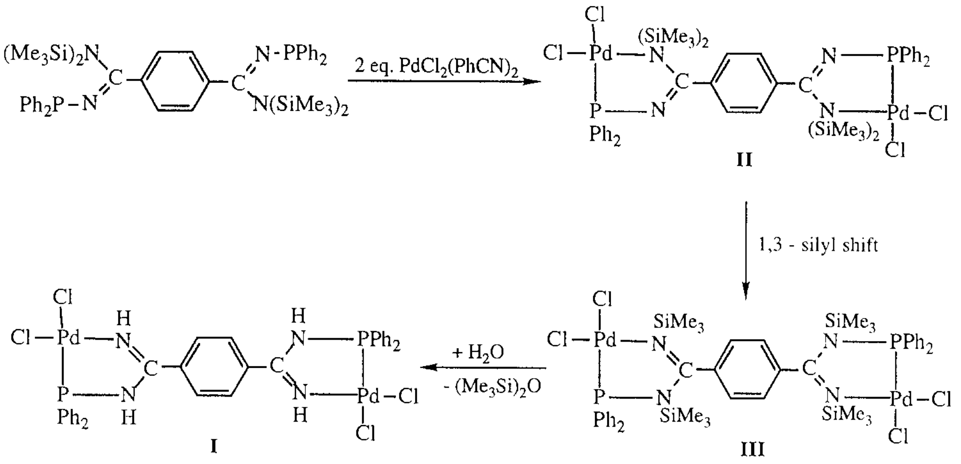
‡ *Crystal data*: $C_{32}H_{28}N_4P_2Cl_4Pd_2 \cdot 6C_3H_7NO$, $Fw = 1323.74$, orthorhombic, $Pba2$ (No. 32), $a = 18.058(2)$, $b = 18.979(2)$, $c = 8.837(1)$ Å, $V = 3028.7(5)$ Å^3, $Z = 2$, $F(000) = 1356$, $D_c = 1.451$ g cm^{-3}, $\mu = 8.76$ cm^{-1}. Crystal dimensions: 0.20 × 0.24 × 0.29 mm. Intensity data were collected on a Rigaku AFC7R diffractometer with graphite monochromated Mo-K_α radiation ($\lambda = 0.71069$ Å) using $\omega - 2\theta$ scans ($2\theta_{max} = 50°$, 3048 unique reflections) at 298 K. The structure was solved by Patterson methods (DIRDIF92 PATTY) after an absorption correction (ψ-scan method, transmission factors 0.974–1.000) was applied and refined by full-matrix least squares to give $R = 0.039$, $Rw = 0.040$ for 2334 independent observed reflections [$I > 3\sigma(I)$]. Pd, P and Cl atoms were refined anisotropically and the rest of the atoms were refined isotropically. Hydrogen atoms were placed in their idealized positions.



Scheme 1. Possible mechanism for the formation of **I**.

produce the final product. A similar mechanism has been proposed for related complexes.[5]

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