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Unexpected N,N′-coordination of tris(2-pyridyl)phosphine chalcogenides to $PdCl_2$

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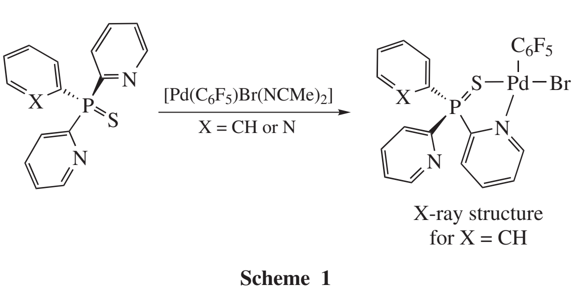
Tris(2-pyridyl)phosphine chalcogenides Py_3P=X (X = O, S, Se) react with $PdCl_2$ or Li_2PdCl_4 to give the chelate complexes *cis*-[Pd(*N*,*N*′-Py_3P=X)Cl_2] in which Pd$^{\mathrm{II}}$ ion is square-planar coordinated to two pyridine nitrogen atoms of the ligand (κ^2-*N*,*N*′).

Pyridylphosphines and their chalcogenides are important polydentate ligands, which find wide applications in catalysis and coordination and organometallic chemistry.[1] Among the pyridylphosphines, tris(2-pyridyl)phosphine is of special interest. Owing to the geminal disposition of nitrogen atoms with regard to the phosphorus atom, this phosphine has rich coordination chemistry.[1,2] At the same time, the coordination abilities of tris(2-pyridyl)phosphine chalcogenides remain unexplored. Thus, based on tris(2-pyridyl)phosphine oxide, only several complexes of sandwich [Fe(*N*,*N*′,*N*″-Py_3P=O)$_2$][3] and semi-sandwich [M(*N*,*N*′,*N*″-Py_3P=O)] (M = W,[4] Rh[5]) types have been prepared. Besides, [Mo(η^3-allyl)Br(CO)$_2$(*N*,*O*-Py_3P=O)][6] and [Rh(COD)(*N*,*N*′-Py_3P=O)](BF$_4$)[5] complexes are known. From phosphine sulfide, one Mo^0 (ref. 7) and one Pd$^{\mathrm{II}}$ (ref. 8) complexes were synthesized, in which N,N′,S- and N,S-coordination, respectively, occurred. Data on tris(2-pyridyl)phosphine selenide complexes are absent at all.

Recent advances[9] in the development of a convenient method for the synthesis of tris(2-pyridyl)phosphine directly from elemental phosphorus and 2-bromopyridine provide an opportunity to develop the coordination chemistry of this phosphine and its chalcogenides. We prepared new Pd$^{\mathrm{II}}$,[9(a)] Co$^{\mathrm{II}}$ [ref. 9(*b*)] and Eu$^{\mathrm{III}}$ (ref. 10) complexes based on available tris(2-pyridyl)phosphine. Here, we report the complexation of $PdCl_2$ toward tris(2-pyridyl)phosphine chalcogenides which are potentially N,N′,N″,X-tetradentate ligands.

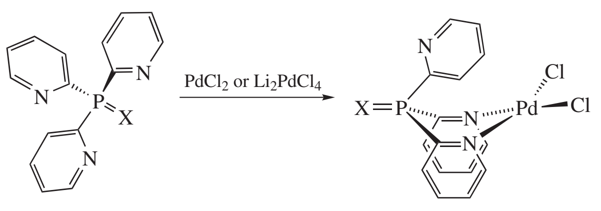
Taking into account published data[8] on the N,S-coordination of tris(2-pyridyl)- and di(2-pyridyl)phenylphosphine sulfides to the Pd$^{\mathrm{II}}$ ion (Scheme 1), we supposed that tris(2-pyridyl)phosphine chalcogenides would exhibit a similar behaviour in complexation with $PdCl_2$.



X-ray structure
for X = CH

Scheme 1

Unexpectedly, we found that tris(2-pyridyl)phosphine oxide and sulfide react with $PdCl_2$ ($CHCl_3$, 50 °C, 8 h) or Li_2PdCl_4 ($CHCl_3$, room temperature, 5–8 min) in a 1:1 molar ratio to afford selectively square-planar Pd$^{\mathrm{II}}$ complexes **1** and **2** (77 and 63% yields, respectively), in which the ligands coordinate the metal center *via* two pyridine nitrogen atoms (Scheme 2).[†] The two potential donor atoms N and O/S in complexes **1**, **2** remain intact, even in an excess of Pd$^{\mathrm{II}}$.



1 X = O (77%)
2 X = S (63%)

Scheme 2

Tris(2-pyridyl)phosphine selenide exhibits low reactivity toward $PdCl_2$ ($CHCl_3$ or MeCN, prolonged heating), meanwhile the reaction with Li_2PdCl_4 (1:1 ratio) readily occurs at ambient temperature (acetone/methanol, 10 min) to give complex [Pd(*N*,*N*′-Py_3P=Se)Cl_2] **3** in 51% isolated yield.[‡]

[†] *Synthesis of complexes* **1** *and* **2**. To a solution of tris(2-pyridyl)phosphine oxide (141 mg, 0.5 mmol) or sulfide (149 mg, 0.5 mmol) in $CHCl_3$ (10 ml), $PdCl_2$ (89 mg, 0.5 mmol) was added. The suspension was stirred at 50 °C for 8 h and then filtered and evaporated. The residue was washed with Et_2O and dissolved in CH_2Cl_2 (30 ml). The slow evaporation of this solution at ambient temperature results in complexes **1** and **2** as monosolvates with CH_2Cl_2. When Li_2PdCl_4 (128 mg, 0.5 mmol) was used instead of $PdCl_2$, the reaction was complete at ambient temperature in 5–8 min.

cis-[Pd(*N*,*N*′-Py_3P=O)Cl_2]·CH_2Cl_2 **1**. Yield 210 mg (77%). Yellow crystals, mp > 150 °C (decomp.). ^{1}H NMR ($CDCl_3$) δ: 5.31 (s, 2H, CH_2Cl_2), 7.63–7.66 (m, 3H, Py), 8.08–8.13 (m, 3H, Py), 8.36 (br. s, 3H, Py), 9.18 (br. s, 3H, Py). ^{31}P{^{1}H} NMR ($CDCl_3$) δ: 18.16. FT-IR (KBr, ν/cm^{-1}): 1588, 1573 (d, $\nu_{\mathrm{C=N}}$), 1452, 1427 (d, $\nu_{\mathrm{C=C}}$), 1214 (s, $\nu_{\mathrm{P=O}}$). UV-VIS ($CHCl_3$, λ_{max}/nm): 264, 376. Found (%): C, 35.49; H, 2.67; N, 7.63. Calc. for $C_{16}H_{14}Cl_4N_3OPPd$ (%): C, 35.36; H, 2.60; N, 7.73.

cis-[Pd(*N*,*N*′-Py_3P=S)Cl_2]·CH_2Cl_2 **2**. Yield 175 mg (63%). Yellow crystals, mp > 130 °C (decomp.). ^{1}H NMR ($CDCl_3$) δ: 5.31 (s, 2H, CH_2Cl_2), 7.61 (br. s, 3H, Py), 8.10 (br. s, 3H, Py), 8.50 (br. s, 3H, Py), 9.14 (br. s, 3H, Py). ^{31}P{^{1}H} NMR ($CDCl_3$) δ: 42.54. FT-IR (KBr, ν/cm^{-1}): 1585, 1572 (d, $\nu_{\mathrm{C=N}}$), 1450, 1424 (d, $\nu_{\mathrm{C=C}}$), 670, 651 (d, $\nu_{\mathrm{P=S}}$). UV-VIS ($CHCl_3$, λ_{max}/nm): 265, 379. Found (%): C, 34.23; H, 2.43; N, 7.34. Calc. for $C_{16}H_{14}Cl_4N_3SPPd$ (%): C, 34.34; H, 2.52; N, 7.51.

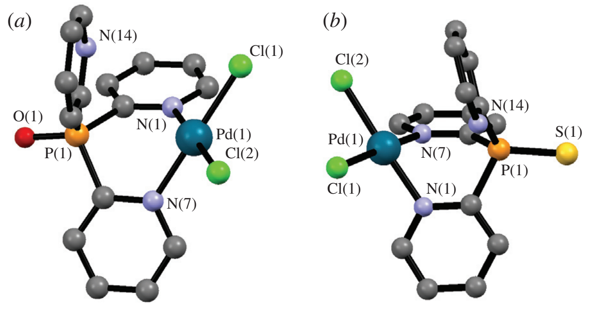
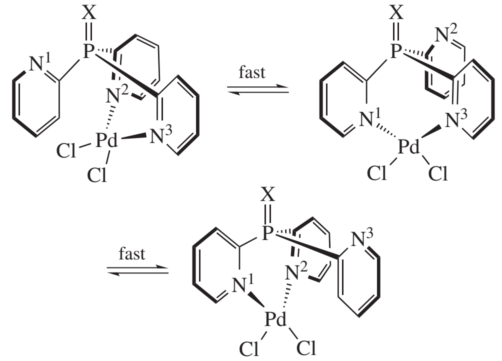


Figure 1 Molecular structures of complexes (*a*) **1** and (*b*) **2** in a crystal state (the H atoms and solvate molecules are omitted for clarity). Selected bond lengths (Å) and angles (°): P(1)–O(1) 1.478(3), P(1)–S(1) 1.9284(9), Pd–Cl 2.279(1)–2.2855(6), Pd–N 2.024(4)–2.046(4), P–C 1.810(5)–1.828(2); Cl(1)–Pd(1)–Cl(2) 91.04(3)–91.07(5), N(7)–Pd(1)–N(1) 89.72(7)–90.2(1).

Complexes **1** and **2** are air-stable crystals moderately soluble in CH_2Cl_2 and $CHCl_3$ and insoluble in water. Conversely, complex **3** is almost insoluble small crystals which are decomposed on air releasing red selenium. The structures of complexes **1**, **2** were established by X-ray diffraction analysis, whereas complex **3** was characterized only by FT-IR, UV-VIS and microanalysis data.

Complexes **1** and **2** crystallize with one solvate CH_2Cl_2 molecule per unit.[§] Their molecular structures reveal a similar geometry (Figure 1). The Pd^{II} ion coordinates two pyridine nitrogen atoms of ligands and two chlorine atoms in the *cis*-positions, exhibiting a slightly distorted square-planar coordination pattern. This is confirmed by the [N–Pd–N] and [Cl–Pd–Cl] angles of ~89.98 and 91.06°, respectively. The maximal deviations from the mean $[PdN_2Cl_2]$ planes are only 0.005 Å (**1**) and 0.066 Å (**2**). Both Pd–N (~2.037 Å) and Pd–Cl (~2.281 Å) bonds are nearly equal in lengths and comparable with these in $[PdPy_2Cl_2]$ complexes.[11] The six-membered chelate ring $[P(–C–N–)_2Pd]$ adopts a boat conformation with torsion angles between the mean P–C–N–Pd planes of 118.0° (**1**) and 117.6° (**2**). A comparison of the P–X (X = O, S) distances in **1** and **2** with those in the free ligands[12,13] shows that the P–O bonds are similar (1.478 and 1.479 Å, respectively), whereas the P–S bond in **2** is slightly shorter than that in tris(2-pyridyl)phosphine sulfide (1.929 *vs.* 1.943 Å).

In solution, all three pyridine cycles within **1** and **2** are equivalent: the ^1H NMR spectra exhibit only four resonances corresponding to pyridine protons. Nevertheless, complexes **1**, **2** are not dissociated since their ^1H and ^{31}P chemical shifts differ significantly from those in free ligands.[13] Probably, the averaging of pyridine signals in the ^1H NMR spectra is caused by an intermolecular 'merry-go-round' rearrangement of complexes **1**, **2**, *i.e.* when the step-by-step cleavage–formation of one Pd–N bond takes place (Scheme 3).



Scheme 3

The UV spectra of complexes **1–3** in $CHCl_3$ show intense absorption bands at 263–265 nm and weak absorptions in the region of 376–379 nm. The high energy bands are assigned to the π–π* intraligand transitions observed in the free ligands (~264 nm), whereas the low energy bands are attributed to dπ–π* transitions specific for square-planar Pd^{II} complexes.[14]

The FT-IR spectra of the complexes are similar (Figure S1, Online Supplementary Materials) except for the strong bands at 1214, 651 and 582 cm^{-1} assigned to P=O, P=S and P=Se stretching in **1–3**, respectively. Notably, though the P=X bonds are non-coordinated to Pd^{II}, their frequencies are shifted to higher wavenumbers compared to the free ligands (1175, 621 and 537 cm^{-1}, respectively[13]). This observation can be explained by a significant difference in the conformations of free and coordinated ligands. The stretching vibrations of the C=N and C=C pyridyl bonds appear as doublet bands at 1572–1588 and 1424–1452 cm^{-1}, respectively. Note that the DFT computations (B3LYP with 6-311+G** and SDD basis sets) well predict the experimental frequencies, especially those associated with P=X vibrations (Table 1).

The DFT computations (the same level) of the isomers of complexes **1–3** also prove that the observable N,N′-coordination of the ligands toward $PdCl_2$ is energetically more preferable than

Table 1 Experimental (FT-IR, solid) and B3LYP/6-311+G(d,p)/SDD simulated selected frequencies for complexes **1–3**.

Complex	ν_{exp}/cm^{-1}	ν_{calc}/cm^{-1}	Mode assignment
1	1588, 1573	1612, 1604	$\nu_{C=N}$ in Py
	1452, 1427	1491, 1482	$\nu_{C=C}$ in Py
	1214	1215	$\nu_{P=O}$
2	1585, 1572	1625, 1611	$\nu_{C=N}$ in Py
	1450, 1424	1489, 1456	$\nu_{C=C}$ in Py
	651	652	$\nu_{P=S}$
3	1581, 1572	1624, 1606	$\nu_{C=N}$ in Py
	1449, 1424	1488, 1458	$\nu_{C=C}$ in Py
	582	567	$\nu_{P=Se}$

[‡] *cis*-$[Pd(N,N'\text{-}Py_3P{=}Se)Cl_2]\cdot CH_2Cl_2$ **3**. A solution of Li_2PdCl_4 (64 mg, 0.25 mmol) in methanol (3 ml) was added to a solution of tris(2-pyridyl)phosphine selenide (86 mg, 0.25 mmol) in CH_2Cl_2 (10 ml). The suspension was stirred at ambient temperature for 10 min and then filtered and cooled at 5–7 °C. The formed crystals were collected and dried *in vacuo* to give 77 mg (51%) of complex **3**. Yellow crystals, mp > 150 °C (decomp.). UV-VIS ($CHCl_3$, λ_{max}/nm): 263, 306. FT-IR (KBr, ν/cm^{-1}): 1581, 1572 (d, $\nu_{C=N}$), 1449, 1424 (d, $\nu_{C=C}$), 582 (br. s, $\nu_{P=Se}$). Found (%): C, 31.60; H, 2.27; N, 6.80. Calc. for $C_{16}H_{14}Cl_4N_3PPdSe$ (%): C, 31.69; H, 2.33; N, 6.93.

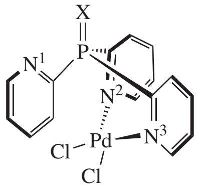
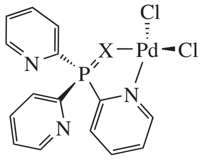
[§] *Crystal data.* For **1**: $C_{16}H_{14}Cl_4N_3OPPd$ (M = 543.47), monoclinic, space group $P2_1/n$ (no. 14), a = 8.6003(9), b = 15.692(2) and c = 15.338(1) Å, β = 92.117(2)°, V = 2068.6(4) Å^3, Z = 4, T = 296(2) K, μ(MoKα) = = 1.502 mm^{-1}, d_{calc} = 1.745 g cm^{-3}, 12217 reflections measured (5.32° ≤ ≤ 2θ ≤ 55.14°), 4674 unique (R_{int} = 0.0442, R_σ = 0.0583), which were used in all calculations. The final R_1 was 0.0453 [$>2\sigma(I)$] and wR_2 was 0.1161 (all data).

For **2**: $C_{16}H_{12}Cl_3N_3PPdS$ (M = 522.07), triclinic, space group $P\bar{1}$ (no. 2), a = 9.1793(7), b = 9.8845(7) and c = 11.7379(9) Å, α = 94.313(1), β = = 108.833(1), γ = 96.769(1)°, V = 993.7(1) Å^3, Z = 2, T = 296(2) K, μ(MoKα) = 1.527 mm^{-1}, d_{calc} = 1.745 g cm^{-3}, 11321 reflections measured (5.24° ≤ 2θ ≤ 60.06°), 5612 unique (R_{int} = 0.0259, R_σ = 0.0407), which were used in all calculations. The final R_1 was 0.0326 [$>2\sigma(I)$] and wR_2 was 0.0765 (all data).

X-ray diffraction analysis was performed on a Bruker SMART APEX-II CCD diffractometer [λ(MoKα) = 0.7107 Å, ω-scans]. The structures were solved by direct methods and the subsequent Fourier syntheses with SHELXS-97 program,[17] and refined by full-matrix least-squares procedures using an anisotropic approximation for all non-H atoms with the SHELXL-97 program.[17] The hydrogen atoms were fixed in ideal geometry positions. An absorption correction was applied using the APEX2 program.[18]

CCDC 981001 and 981002 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

Table 2 The relative energies and free Gibbs energies (in parentheses) for N,N′- and N,X-isomers of complexes **1**–**3** from B3LYP/6-311+G(d,p)/SDD computations.

Structure	X		
	O	S	Se
	0.00	0.00	0.00
	1.81 (9.55)	7.60 (5.19)	6.77 (4.84)

the alternative N,X-mode by 11.81, 7.60 or 6.77 kcal mol^{-1} for X = O, S or Se, respectively (Table 2). The destabilization of N,X-isomers may be caused by the five-membered chelate rings which possess a higher strain energy than the six-membered rings within observable N,N′-isomers. The computed geometries of complexes **1**, **2** correlate well with their X-ray structures.

In summary, the unexpected N,N′-chelating mode of tris-(2-pyridyl)phosphine chalcogenides in new square-planar $\mathrm{Pd^{II}}$ dichloride complexes has been disclosed. These ligands coordinate to the metal in an approximately isobidentate manner to form six-membered P(–C–N–)$_2$Pd rings having a boat conformation. The obtained $\mathrm{Pd^{II}}$ derivatives are prospective anti-cancer chemotherapeutics[15] and catalysts for cross-coupling reactions.[16]

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2015.05.012.

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