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First example of pyrrole-2-carbaldehyde thiosemicarbazone as tridentate dianion in [Pd(η^3-N^4,N^3,S-ptsc)(PPh_3)] complex

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Abstract

Reaction of pyrrole-2-carbaldehyde thiosemicarbazone (H_2ptsc) with $PdCl_2(PPh_3)_2$ in 1:1 mol ratio in presence of Et_3N leads to complete dechlorination to generate square planar complex, [Pd(η^3-N^4,N^3,S-ptsc)(PPh_3)] (**1**), existing as three independent molecules in the same unit cell, and H_2ptsc behaves in an unusual dinegative tridentate mode. Salicylaldehyde thiosemicarbazone (H_2stsc) formed similar compound, [Pd(η^3-O,N^3,S-stsc)(PPh_3)] (**3**).

Keywords: Pyrrole-2-carbaldehyde thiosemicarbazone; Palladium(II); Triphenyl phosphine; Dechlorination

Pyrrole-2-carbaldehyde thiosemicarbazone (H_2ptsc) has several potential donor sites, and thus binds to metals as a neutral ligand in η^1-S terminal [1,2], or η^2-N^3,S-chelating bonding modes [3]. Further, it acts as N^3,S-chelating anionic ligand after loss of hydrazinic (–N^2H) proton [3–5]. In all the cases reported, pyrrole ring at C^2 carbon remains pendant, and there is no example to date in which a metal activates pyrrole (–NH) hydrogen to form M–N bonds [1–5], except removal of this hydrogen by a strongly basic alkyl group of a metal alkyl [6]. On the other hand, pyridine substituent at C^2 carbon is well known to coordinate to metals, such as in [Pd(η^3-N^4,N^3,S-pytsc)Cl] (**2**) (Hpytsc = pyridine-2-carbaldehyde thiosemicarbazone), prepared by the reaction of Li_2PdCl_4 with Hpytsc in methanol [7].

Reaction of $[PdCl_2(PPh_3)_2]$ with Hpytsc in 1:1 and 1:2 ratios in presence of Et_3N, designed to prepare stepwise [PdCl(pytsc)(PPh_3)], and [Pd(pytsc)$_2$] complexes, invariably formed compound [Pd(η^3-N^4,N^3,S-pytsc)Cl] **2**. It showed strong tendency of pytsc$^-$ ligand to act as a tridentate with removal of both phosphine ligands. These observations increased our curiosity to study the comparative behaviour of pyrrole-2-carbaldehyde thiosemicarbazone, which has pendant (–N^4H) nitrogen, and could be a N^4-donor, if deprotonation occurs at this center. Interestingly, reaction of $[PdCl_2(PPh_3)_2]$ with H_2ptsc in toluene in presence of Et_3N in 1:1 and 1:2 mol ratios, invariably formed compound of stoichiometry, [Pd(ptsc)(PPh_3)] (**1**). This is an unusual reaction in which both halogens and one PPh_3 ligand are removed along with deprotonation of hydrazinic (–N^2H) and pyrrole ring (–N^4H) protons, the comparative behaviour of salicylaldehyde thiosemicarbazone is also described and these findings are reported in this communication. In literature, pyrrole ring is known to undergo deprotonation and subsequently bind to a metal center in porphyrins and some other class of ligands [8].

Scheme 1 depicts the formation of compound **1**, alongwith formation of compounds **2** and **3**. Reaction of $PdCl_2(PPh_3)_2$ [9] with one mole of H_2ptsc, in presence of Et_3N base, in toluene gave complex [Pd(ptsc)(PPh_3)] (**1**); same product resulted with two moles of H_2ptsc ligand.

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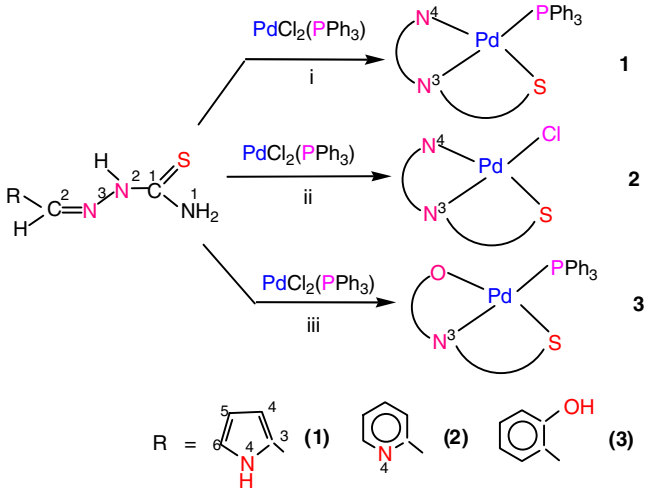

Scheme 1. (i–iii) Toluene Et_3N.

The crystal structure of complex **1** (Fig. 1) reveals that Pd is coordinated to one thiosemicarbazone ligand via N^4,N^3 and S donor atoms after deprotonation of $-N^2H$ and $-N^4H$ protons. The reaction appears to occur in a systematic manner in presence of Et_3N base, resulting in removal of both Cl^- ions as insoluble $Et_3NH^+Cl^-$ salt in toluene. Due to tridentate binding of the thiosemicarbazone ligand, one of the $-PPh_3$ group is also removed from the metal center. Complex **1** is soluble in toluene, methanol, dichloromethane and chloroform. Compound **3** with salicylaldehyde thiosemicarbazone (H_2stc) was prepared similarly.

Compound **1** showed three types of molecules (A, B, C) with different bond parameters (Table 1). In molecule (A), palladium(II) is bonded to two N atoms at bond distances of

Table 1
Bond parameters {bond distances (Å) and bond angles (°)} of three molecules (A, B, C) of compound **1**

	A	B	C
Pd–N12, Pd–N11	2.005(4), 2.029(4)	2.009(4), 2.037(4)	2.016(4), 2.039(4)
Pd–P, Pd–S	2.2364(13), 2.2566(13)	2.2596(13), 2.2577(13)	2.2617(11), 2.2543(14)
N12–Pd–N11	80.79(16)	80.13(16)	80.10(17)
N12–Pd–P	176.53(11)	177.37(12)	177.90(11)
N11–Pd–P	99.90(12)	102.09(11)	98.36(12)
N12–Pd–S	83.44(11)	83.34(12)	83.30(13)
N11–Pd–S	164.22(12)	163.46(11)	163.39(12)
P–Pd–S	95.82(4)	94.45(5)	98.23(5)

2.005(4) ($Pd–N12_{azomethine}$) and 2.029(4) Å ($Pd–N11_{pyrrole}$), with Pd–P bond distance of 2.2364(13) Å. In molecules (B) and (C), the corresponding distances are marginally longer; however, Pd–S distances are almost identical for the three molecules. These distances are comparable with analogous Pd^{II} complexes with tridentate pyridine-2-carbaldehyde thiosemicarbazones {N^4,N^3, S-donors} [10,7]. The bite angles N12–Pd–N11 and N12–Pd–S marginally decrease from molecules A to C. The *trans* N12–Pd–P bond angles, ca. 177–178° are close to linearity, while N11–Pd–S angles ca. 164° significantly deviate from linearity. The difference in bond parameters is attributed to different hydrogen bond interactions. For example, molecule A forms centrosymmetric dimers with two identical N–H···N hydrogen bonds, whereas molecules B and C interact mutually and form different types of hydrogen bonds.

In compound **3**, Pd^{II} is coordinated to O, N^3 and S atoms of salicylaldehyde thiosemicarbazone ligand, and the fourth site is occupied by PPh_3 ligand (Fig. 2). The Pd–N {2.0190(13) Å}, Pd–S {2.2453(4) Å} and Pd–P {2.2756(4) Å} distances are comparable to those of com-

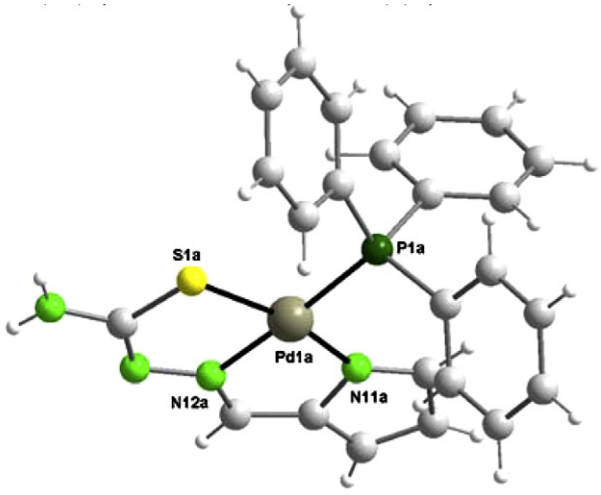

Fig. 1. Structure of complex **1** (molecule A) with atomic numbering scheme. Selected bond lengths (Å) and angles (°): Pd(1A)–N(12A) 2.005(4), Pd(1A)–N(11A) 2.029(4), Pd(1A)–P(1A) 2.2364(13), Pd(1A)–S(1A) 2.2566(13) and N(12A)–Pd(1A)–N(11A) 80.79(16), N(12A)–Pd(1A)–P(1A) 176.53(11), N(11A)–Pd(1A)–P(1A) 99.90(12), N(12A)–Pd(1A)–S(1A) 83.44(11), N(11A)–Pd(1A)–S(1A) 164.22(12), P(1A)–Pd(1A)–S(1A) 95.82(4).

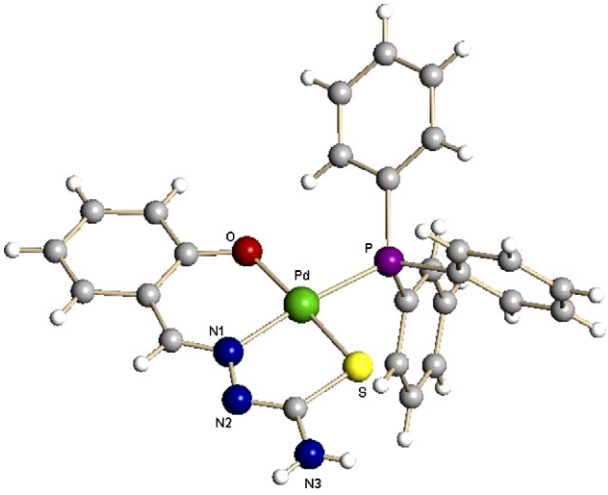

Fig. 2. Structure of complex **3** with atomic numbering scheme. Selected bond lengths (Å) and angles (°) : Pd–O, 2.0170(13), Pd–N(1) 2.0190(13), Pd–S 2.2453(4), Pd–P 2.2756(4) and O–Pd–N(1) 92.99(5), O–Pd–S 177.14(4), N(1)–Pd–S 84.16(4), O–Pd–P 91.08(4), N(1)–Pd–P 173.99(4), S–Pd–P 173.99(4).

plex **1.** The N12A–Pd–S bite angle in complexes **1** and N1–Pd–S angle of **3** are similar, whereas N12A–Pd–N11A {80.79(16)°} bite angle of **1** and O–Pd–N1 {92.99(5)°} angle of **3** are quite different. This may be attributed to the fact that in **1** the N donor atom is part of the five membered pyrrole ring, whereas in complex **3** the O atom is exocyclic. Thus system **1** is more strained as compared to **3**, this also explains the difference in *trans* angles N11A–PdA–S1A {164.22(12)°} and O–Pd–S {177.14(4)°}.

^{1}H NMR spectrum of compounds **1** and **3** were recorded in $CDCl_3$. In the spectrum of complex **1**, the absence of –N^2H and –N^4H hydrogens, at 11.28 and 11.34 ppm respectively for free ligands [4], confirmed their deprotonation, followed by coordination to Pd center as a dianion. Other characteristic peaks of the thiosemicarbazone ligand are: C^2H 5.65(s), C^5H(q) 5.80, C^4H(dd) 6.49, C^6H(d) 7.18 ppm. In addition, PPh_3 ring peaks also appear in the spectra in the region, 7.48–7.67 ppm. The ^{31}P NMR spectrum shows a single peak at −79.2 ppm with a coordination shift, $\Delta\delta(\delta_{complex}-\delta_{ligand}) = 33.9$ ppm, supporting coordination of P atom to Pd. In the IR spectrum, the ν(N–H) band due to –N^2H– moiety appears at 3152 cm^{-1} in the free ligand, which is absent in complex **1**. Similarly for complex **3**, the spectrum showed the absence of –OH and –N^2H proton signals {cf. –OH, 9.87 and –N^2H, 11.38 ppm, free ligand}, confirming double deprotonation. ^{31}P NMR also showed a single peak with a coordination shift of 30.08 ppm.

As depicted in Scheme 1, the deprotonation of acidic hydrogen such as –N^4H and –OH in rings at C^2 carbon facilitates tricoordination by the thiosemicarbazone as dianions in **1** and **3**, thus retaining one PPh_3 ligand, while lack of acidic hydrogen as in **2**, retains one Cl and not PPh_3 in view of overall charge balance. The Cl in **2** is not appearing as anion such as in anticipated, [Pd(η^3-N^4,N^3,S-pytsc)(PPh_3)]Cl, thus presumably {Pd(η^3-N^4, N^3, S-pytsc)} species has strong affinity to bring Cl in coordination sphere, leading to exit of PPh_3.

In conclusion, an acidic hydrogen in the ring has important role in determining coordination modes of thiosemicarbazones, and tricoordination by pyrrole-2-carbaldehyde thiosemicarbazone (H_2ptsc) is first example.

Compound **1**: Mp. 240–242 °C (dec.), yield: 0.025 g, 62%. C, H, N, analysis for $C_{24}H_{21}N_4PPdS$: C, 53.9; H, 3.92; N, 10.48; Found: C, 53.5; H, 3.64; N, 9.51. Main IR Peaks (KBr, cm^{-1}): ν(N–H), 3463m, 3342m, 3280m (–NH_2); ν(C–H), 3072w; $\delta(NH_2) + \nu$(C=N) + ν(C–C), 1600m, 1566s, 1517s; ν(C=S) + ν(C–N), 1033s, 1000w, 850w (thioamide moiety). **3**: Mp. 230–232 °C, yield: 0.025 g, 60%;. C, H, N, analysis for $C_{26}H_{22}N_3OSPPd$: C, 55.61; H, 3.92; N, 7.50; Found: C, 55.74; H, 3.89; N, 7.81. Main IR peaks (KBr, cm^{-1}), ν(NH) 3438s, ν(C–H) 3101m, ν(C=N) + δNH_2 + ν(C=C) 1635m, 1591s, 1529s, ν(C=S) 939w, ν(P–C) 1097s ^{1}H NMR data (δ, ppm; $CDCl_3$), 8.25 (d, 1H, C^2H), 4.71 (s, 2H, NH_2), 6.60–6.69 (m, 1H, C^5H), 7.40–7.78 (17H, Ph-H + $C^{4,6}$) ppm. ^{31}P NMR data (δ, ppm, $CDCl_3$), −83.073 ppm, $\Delta\delta(\delta_{complex}-\delta_{ligand}) = 30.08$ ppm (^{31}P NMR spectra were recorded by taking TMP {$(MeO)_3P$} as external reference taken at zero position).

Crystallographic data for **1**: $C_{24}H_{21}N_4PPdS$, $M = 534.88$, triclinic, $a = 10.307(2)$ Å, $b = 14.962(3)$ Å, $c = 24.351(5)$ Å, $\alpha = 100.908(4)°$, $\beta = 99.508(4)°$, $\gamma = 107.255(3)°$, $V = 3422.0(12)$ Å^3, $T = 293(2)$ K, space group $P\bar{1}$ (No. 2), $\rho_{calcd} = 1.557$ g cm^{-3}, $Z = 6$, μ(Mo Kα) = 0.994 mm^{-1}, 21,136 reflections measured on a Bruker SMART CCD-1000 diffractometer unique 15,007 ($R_{int} = 0.0382$). The final R_1 0.0490 was for 10,152 reflections [$I > 2\sigma(I)$] and wR_2 was 0.1233. Crystals **3**. $C_{26}H_{22}N_3OPPdS$', $M = 561.90$, Triclinic, $a = 7.5551(2)$, $b = 10.2388(3)$, $c = 17.0045(5)$ Å, $\alpha = 77.04$, $\beta = 80.8980(10)$, $\gamma = 71.54°$, $V = 1210.52(6)$ Å^3, $T = 298(2)$ K, space group $P\bar{1}$ (No. 2), $\rho_{calcd} = 1.542$ g cm^{-3}, $Z = 2$, μ(Mo Kα) = 0.943 mm^{-1}, 13,980 reflections measured on a Bruker SMART CCD-1000 diffractometer unique 6826 ($R_{int} = 0.0146$). The final R_1 0.0246 was for 6203 reflections [$I > 2\sigma(I)$] and wR_2 was 0.0639.

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Appendix A. Supplementary material

CCDC 627413 and 627414 contain the supplementary crystallographic data for **1** and **3**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.htmlor from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2006.12.024.

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