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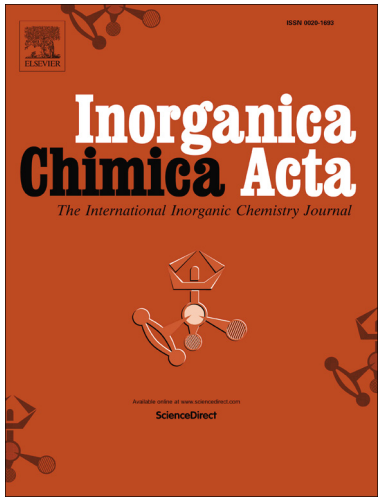

Research paper

A comparative study of the coordination of saccharinate, thiosaccharinate and benzisothiozolinate ligands to cyclometalated [Pd($Me_2NCH_2C_6H_4$ -κ^2N,C)(μ-Cl)]$_2$: Molecular structures of [Pd($Me_2NCH_2C_6H_4$ -κ^2N,C)(μ-X)]$_2$ (X = sac, bit and tsac) and [Pd($Me_2NCH_2C_6H_4$ -κ^2N,C)Cl(ampyH-κ^1N)] (ampyH = 2-amino-3-methylpyridine)

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A comparative study of the coordination of saccharinate, thiosaccharinate and benzisothiozolinate ligands to cyclometalated [Pd($Me_2NCH_2C_6H_4$-κ^2N,C)(μ-Cl)]$_2$: Molecular structures of [Pd($Me_2NCH_2C_6H_4$-κ^2N,C)(μ-X)]$_2$ (X = sac, bit and tsac) and [Pd($Me_2NCH_2C_6H_4$-κ^2N,C)Cl(ampyH-κ^1N)] (ampyH = 2-amino-3-methylpyridine)

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Abstract

Reactions of [Pd($Me_2NCH_2C_6H_4$-κ^2N,C)(μ-Cl)]$_2$ with two equivalents of sodium saccharinate (Nasac), thiosaccharin (Htsac) or sodium benzisothiozolinate (Nabit) results in the stepwise substitution of the bridging halides to form sequentially [Pd_2($Me_2NCH_2C_6H_4$-κ^2N,C)$_2$(μ-Cl)(μ-X)] (X = sac, tsac) and [Pd($Me_2NCH_2C_6H_4$-κ^2N,C)(μ-X)]$_2$ (X = sac, tsac, bit). The molecular structures of all three disubstituted complexes are reported. In each the two metalated ligands bind in a chelate manner adopting a relative *anti* conformation, while the new ligands bridge the two palladium atoms adopting a relative *cis* conformation. The local conformation about each palladium differs with small ligand changes. Thus in the sac and bit complexes all nitrogens lie *trans* to one another, in the tsac complex they are *cis*. Conformational changes also lead to large differences in the non-bonded Pd…Pd distance which range over 0.5 Å. Treatment of [Pd($Me_2NCH_2C_6H_4$-κ^2N,C)(μ-Cl)]$_2$ with two equivalents of 2-amino-3-methylpyridine (ampyH) in the presence of NEt_3 affords mononuclear [PdCl($Me_2NCH_2C_6H_4$-κ^2N,C)(ampyH-κ^1N)] as a result of "bridge-splitting", the

ampyH ligand binding through the pyridyl-nitrogen and lying approximately perpendicular to the $PdCClN_2$ plane as shown by a crystallographic study.

Keywords: dipalladium; cyclometalated; saccharinate; thiosaccharinate; benzisothiozolinate

1. Introduction

Saccharinate (sac) is a versatile poly-functional ligand, shown to adopt a variety of coordination modes, and consequently its coordination chemistry has been widely studied [**1**]. The coordination chemistry of thiosaccharinate has also received recent attention [**2-18**], but that of benzisothiozolinate (bit) remains virtually unexplored [**19-20**] (**Chart 1**). With this in mind we recently reported a comparative study of the reactions of each of these ligands with *trans*-$[PdCl_2(H_2NBz)_2]$ [**21**]. The expected outcome of this was that in each case both chlorides could be replaced by the new ligands (and indeed even addition of one equivalent of ligand gave the disubstituted product), the unexpected outcome was the isolation of three different product types. With sodium saccharinate, *trans*-$[Pd(N\text{-}sac)_2(H_2NBz)_2]$ resulted in which the sac ligands are N-bound and while a similar N-bound coordination was observed with sodium benzisothiazolinate, substitution also resulted in a relative rearrangement of the two amine ligands leading to formation of *cis*-$[Pd(N\text{-}bit)_2(H_2NBz)_2]$. In contrast, with sodium thiosaccharinate the new ligands adopted an S-bound coordination mode affording *trans*-$[Pd(S\text{-}tsac)_2(H_2NBz)_2]$ [**21**].

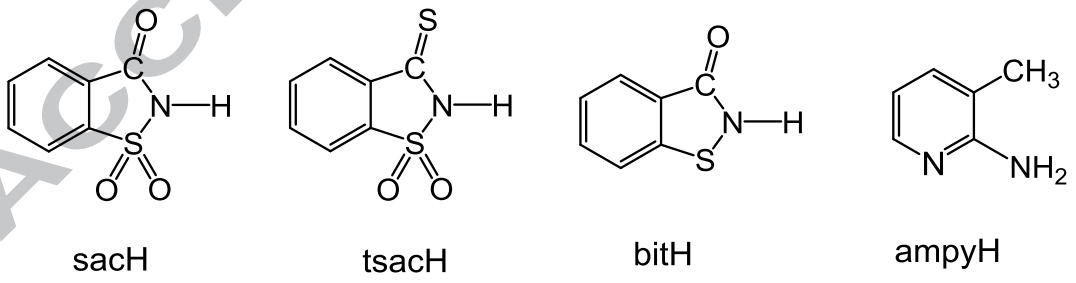

Chart 1. Ligands used in this work

Palladium complexes find widespread applications in homogeneous catalysis with those containing cyclic metalated chelating ligands (termed palladacycles) being particularly prevalent [**22-26**]. An early example of such a complex is binuclear $[Pd(Me_2NCH_2C_6H_4\text{-}$

κ^2N,C)(μ-Cl)]$_2$ (**1**) prepared by Cope and Friedrich in 1968 [**27**] and subsequently widely studied [**28-36**]. Classic reactivity patterns of **1** include so-called "bridge-splitting" upon addition of two equivalents of a monodentate neutral ligand (L) to yield mononuclear complexes of the type [Pd($Me_2NCH_2C_6H_4$-κ^2N,C)Cl(L)], while with bidentate monocharged ligands (LX) either mononuclear [Pd($Me_2NCH_2C_6H_4$-κ^2N,C)(LX-κ^2)] or binuclear [Pd($Me_2NCH_2C_6H_4$-κ^2N,C)(μ-LX)]$_2$ result [**28**]. Examples of the latter include reactions with acetate [**37**] and tetrafluoroacetate [**29**] which afford [Pd($Me_2NCH_2C_6H_4$-κ^2N,C)(μ-O_2CMe)]$_2$ and [Pd($Me_2NCH_2C_6H_4$-κ^2N,C)(μ-O_2CCF_3)]$_2$ respectively, while related carboxamide complexes [Pd($Me_2NCH_2C_6H_4$-κ^2N,C)(μ-HNCRO)]$_2$ are also readily accessible [**30**]. Continuing our studies on the coordination chemistry of the closely related sac, tsac and bit ligands, we herein report the outcomes of their reactions with **1**. We show that all three ligands behave in an analogous fashion to afford disubstituted [Pd($Me_2NCH_2C_6H_4$-κ^2N,C)(μ-X)]$_2$ (X = sac, tsac, bit) (**2-4**) as the final products, while for sac and tsac the intermediate mono-substituted complexes [Pd$_2$($Me_2NCH_2C_6H_4$-κ^2N,C)$_2$(μ-Cl)(μ-X)] (X = sac, tsac) (**5-6**) are also accessible. All three disubstituted derivatives have been crystallographically characterised allowing metric parameters to be compared and significant structural differences to be identified. We also detail the synthesis and crystal structure of [PdCl($Me_2NCH_2C_6H_4$-κ^2N,C)(ampyH-κ^1N)] (**7**), formed from the bridge-splitting reaction of **1** with 2-amino-3-methylpyridine (ampyH) (**Chart 1**).

2. Experimental

2.1. General methods, reagents and instrumentation

^{1}H NMR spectra were recorded on a Varian Unity spectrometer using d^6-DMSO as solvent. IR spectra were recorded on Shimadzu FT-IR 8400 spectrophotometer in the 400-4000 cm^{-1} range as KBr discs and in the 200-600 cm^{-1} as CsI discs Elemental analyses were carried out at Al Al-Bayt University, Jorden using a Euro vector EURO EA300 elemental analyser. Melting points measured on a Gallenkamp melting point apparatus and are uncorrected. Conductivity measurements were carried out on 10^{-3} molar solutions using a digital conductivity meter. Benzisothiazoline (Hbit), sodium saccharinate (Nasac) and 2-amino-3-methylpyridine (ampy) are commercial products used as received. [Pd($Me_2NCH_2C_6H_4$-

κ^2N,C)(μ-Cl)]$_2$ (**1**) [**27**], 2-acetylamino-3-methylpyridine (acmpy) [**38**], thiosaccharin (Htsac) [**39**] and sodium benzisothiozolinate (Nabit) [**19**] were prepared by literature methods.

2.2. Synthesis of [Pd(Me$_2$NCH$_2$C$_6$H$_4$-κ^2N,C)(μ-sac)]$_2$ (2)

A solution of Nasac (0.037 g, 0.18 mmol) in MeOH (3 cm^3) was added to a solution of **1** (0.050 g, 0.09 mmol) in $CHCl_3$ (8 cm^3). The mixture was stirred at room temperature for 2 h, filtered and left to evaporate. The lemon-yellow solid which formed was filtered off, washed with water and dried under vacuum. Yield 0.062 g, 88%. *Anal*. Calc. for $C_{33}H_{32}N_4O_6Pd_2S_2$: C, 45.4, H, 3.8, N, 6.6. Found: C, 46.0, H, 4.0, N, 6.5. Molar conductivity (DMSO): 1.00 (Ω^{-1} mol^{-1} cm^{-1}). IR: 3051w, 2918w, 1623s, 1585s, 1452m, 1257s, 1172s, 536m cm^{-1}. ^{1}H NMR (DMSO-d^6): δ 7.93 (dd, J 8.0, 2H, sac), 7.78 (d, J 7.6, 4H, sac), 7.56 (d, J 7.6, 2H, sac), 7.08 (d, J 3.6, 2H, Ph), 7.02 (bs, 2H, Ph), 6.85 (t, J 8.0, 2H, Ph), 6.61 (t, J 8.0, 2H, Ph), 4.06 (bs, 2H, CH_2), 3.95 (bs, 2H, CH_2), 2.70 (s, 12H, 4CH_3). Mp: 198-200^{o}C.

2.3. Synthesis of [Pd(Me$_2$NCH$_2$C$_6$H$_4$-κ^2N,C)(μ-tsac)]$_2$ (3)

A solution of Htsac (0.035 g, 0.18 mmol) in MeOH (3 cm^3) was added to a solution of **1** (0.051 g, 0.09 mmol) in $CHCl_3$ (10 cm^3). The mixture was stirred at room temperature for 2 h to afford an orange precipitate which was collected and dried. Recrystallisation from acetone/MeOH gave orange needle-like crystals. Yield 0.072 g, 91%. *Anal*. Calc. for $C_{35}H_{39}N_5O_5Pd_2S_4$: C, 44.8, H, 3.7, N, 6.4. Found: C, 44. 5, H, 3.8, N, 6.3. Molar conductivity (DMSO): 0.80 (Ω^{-1} mol^{-1} cm^{-1}). IR: 3040w, 2921w 1560s, 1452vs, 1317s, 1168m, 1018s, 815m, 439w cm^{-1}. ^{1}H NMR (DMSO-d^6): δ 8.12-8.10 (m, 2H, tsac), 7.97-7.9 (m, 2H, tsac), 7.83 (dd, J 7.6, 1.2, 4H, tsac), 7.46 (dd, J 7.6, 1.2, 2H, Ph), 7.04 (dd, J 7.2, 1.2, 2H, Ph), 6.98 (dd, J 7.2, 1.2, 2H, Ph), 6.82 (dd, J 7.19, J 1.19, 2H, Ph), 4.12 (s, 4H, 2CH_2), 2.72 (s, 12H, 4CH_3). Mp: 244-246 ^{o}C.

2.4. Synthesis of [Pd(Me$_2$NCH$_2$C$_6$H$_4$-κ^2N,C)(μ-bit)]$_2$ (4)

To a solution of Nabit (0.068 g. 0.36 mmol) in MeOH was added **1** (0.10 g, 0.18 mmol) in $CHCl_3$ (10 cm^3). The mixture was stirred at room temperature for 2 h and then filtered. The filtrate was set aside to evaporate at room temperature and the resulting orange needles were

collected and dried under vacuum. Yield 0.126 g, 88%. *Anal.* Cal. For $C_{33}H_{33}Cl_3N_4O_2Pd_2S$: C, 49.2, H, 4.1, N, 7.2. Found: C, 49.4, H, 4.4, N, 7.0. Molar conductivity (DMSO): 0.80 (Ω^{-1} mol^{-1} cm^{-1}). ^{1}H NMR (DMSO-d^6): δ 7.78 (s, 4H, bit), 7.48 (s, 2H, bit), 7.28 (s, 2H, bit), 6.94 (s, 4H, Ph), 6.73 (s, 2H, Ph), 6.48 (d, J 8.0, 2H, Ph), 4.03 (s, 4H, $2CH_2$), 2.72 (s, 12H, $4CH_3$). IR: 3051w, 2910w, 1650s, 1533s, 1444m, 516m cm^{-1}. Mp: 222-224°C.

2.5. Synthesis of [$Pd_2(Me_2NCH_2C_6H_4$-κ^2N,C)$_2$(μ-Cl)(μ-sac)] (5)

A solution of Nasac (0.037 g, 0.18 mmol) in MeOH (3 cm^3) was added to a solution of **1** (0.10 g, 0.18 mmol) in $CHCl_3$ (8 cm^3). The mixture was stirred at room temperature for 2 h. The off-white solid formed was collected, washed with water and dried under vacuum. Yield 0.112 g, 88%. Anal. Calc. for $C_{25}H_{28}ClN_3O_3Pd_2S$: C, 43.0, H, 4.0, N, 6.0. Found: C, 42.5, H, 4.2, N, 5.9. Molar conductivity (DMSO): 1.20 (Ω^{-1} mol^{-1} cm^{-1}). IR: 1630vs, 1556vs, 1450m, 1257vs, 1168s, 527m, 364s cm^{-1}. ^{1}H NMR (DMSO-d^6): δ 7.97 (d, J 7.6, 2H, sac), 7.91 (d, J 7.6, H, sac), 7.81-7.75 (m, 2H, sac), 7.59 (d, J 7.6, 2H, sac), 7.03 (bs, 2H, Ar), 6.94 (bs, 2H, Ar), 6.85 (t, J 8.4, 2H, Ar), 6.61 (t, J 8.0, 2H, Ar), 4.03 (s, 4H, $2CH_2$), 2.68 (s, 12H, $4CH_3$). Mp: 226-228°C.

2.6. Synthesis of [$Pd_2(Me_2NCH_2C_6H_4$-κ^2N,C)$_2$(μ-Cl)(μ-tsac)] (6)

A solution of Htsac (0.035g, 0.18mmol) in MeOH was added to a solution of **1** (0.10g, 0.18 mmol) in $CHCl_3$ (10 cm^3). The mixture was stirred for 2 h and the resulting pale brown solid was collected and dried in vacuum. Yield 0.116 g, 90%. *Anal*. Calc. for $C_{25}H_{28}ClN_3O_2Pd_2S_2$: C, 42.0, H, 4.0, N, 5.9. Found: C, 42.2, H, 4.0, N, 5.7. Molar conductivity (DMSO): 0.30 (Ω^{-1} mol^{-1} cm^{-1}). IR: 3083w, 2916w, 1558m, 1453vs, 1317s, 1168s, 1020s, 815s, 449w, 362s cm^{-1}. ^{1}H NMR (DMSO-d^6): δ 8.12-8.10 (dd, J 7.2, 1.2 2H, Ph), 7.97-7.95 (m, 1H, Ph), 7.84-7.82 (m, 2H, Ph), 7.60 (d, J 7.2, 1H, Ph), 7.47 (d, J 7.2, 1H, Ph), 7.05- 6.91 (m, 5H, Ph), 6.82 (d, J 7.2, 1H, Ph), 4.02 (s, 4H, CH_2), 2.72 (s, 12H, $4CH_3$). Mp: 202-204°C.

2.7. Synthesis of [Pd($Me_2NCH_2C_6H_4$-κ^2N,C)Cl(ampyH-κ^1N)] (7)

A solution of 2-amino-3-methylpyridine (ampyH) (0.54 g, 0.36 mmol) in MeOH was added to a solution of **1** (0.10 g, 0.18 mmol) in $CHCl_3$ (10 cm^3). Three drops of NEt_3 were added

and the mixture was stirred at room temperature for 3 h. It was then filtered and the filtrate was left to evaporate at room temperature to afford pale yellow needles. These were collected by filtration, washed with warm water and dried under vacuum. Yield 0.066 g, 91%. *Anal*. Calc. for $C_{15}H_{20}ClN_3Pd$: C, 46. 9, H, 5.5, N, 10.9. Found: C, 47.1, H, 5.5, N, 11.1. Molar conductivity (DMSO): 0.40 (Ω^{-1} mol^{-1} cm^{-1}). IR: 3296m, 3026w, 2918w, 1568s, 1515s, 518m, 352m cm^{-1}. ^{1}H NMR (DMSO-d^6): δ 8.07 (d, J 6.0, 1H, Py), 7.43 (d, J 6.7, 1H, Py), 6.97-6.85 (m, 3H, 1Py+2 Ph), 6.61 (m, 2H, Ph), 5.78 (s, 2H, NH_2), 4.01 (dt, J 6.0, 2H, CH_2), 2.76 (t, J 6.7, 6H, $2CH_3$), 2.34 (s, 3H, Py-CH_3). Mp: 196-198^{o}C.

2.8. Molecular structure determinations

Crystals of suitable for X-ray crystallography were mounted on a glass fiber and all geometric and intensity data were taken from this sample using a STOE-IPDS diffractometer (**2-4**) or Oxford Diffraction Supernova with Atlas detector (**7**) with Mo-Kα radiation (λ = 0.7103 Å, graphite monochromator). Absorption corrections were made using the IPDS software package [**40**]. All structures were solved by direct methods and refined using full-matrix least-square routines against F^2 with SHELXL-97 [**41**]. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in the models by calculating the positions (riding model) and refined with calculated isotropic displacement parameters. Illustrations were generated using DIAMOND 3.0 [**42**]. Crystallographic data is summarised in Table 1.

3. Results and discussion

3.1. Synthesis and characterisation of disubstituted [Pd($Me_2NCH_2C_6H_4$-κ^2N,C)(μ-X)]$_2$ (X = sac, tsac, bit)

Addition of two equivalents of methanol solutions of Nasac, tsacH or Nabit to [Pd($Me_2NCH_2C_6H_4$-κ^2*N,C*)(μ-Cl)]$_2$ in $CHCl_3$ at room temperature resulted in the slow (2-3 h) formation of disubstituted [Pd($Me_2NCH_2C_6H_4$-κ^2*N,C*)(μ-X)]$_2$ (X = sac, tsac, bit) (**2-4**) in 88-91 % yields as air and moisture stable yellow-orange solids. Analytical and spectroscopic data were in full accord with the proposed formulations and these were confirmed in each case by X-ray crystallographic studies the results of which are summarised in Figures 1-3 and

their captions. Complex **3** crystallises with a molecule of dmf and **4** with a molecule of $CHCl_3$. In the latter there is a short contact between a chloride and an oxygen [Cl(1)···O(1) 3.22 Å] but this does not influence the overall structure. While the three complexes are superficially similar closer inspection reveals that each has unique features and the saccharinate complex **2** is markedly different from thiosaccharinate and benzisothiozolinate complexes **3** and **4** respectively.

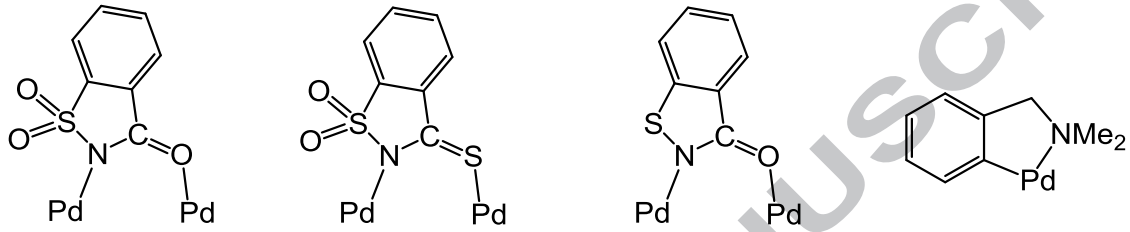

Chart 2. Binding modes of ligands used in this work

In all three complexes the cyclometalated N,N,-dimethylbenzylamine ligands bind in a chelate manner the cyclometalated ligands adopting a relative *anti* configuration, which is common for complexes of this type [**29,30,43-46**]. The introduced ligands bridge the dipalladium centre, binding in all cases through nitrogen and either the carbon oxygen (sac and bit) or thiocarbonyl sulfur (tsac) (**Chart 2**) lying *cis* to one another (**Chart 3**).

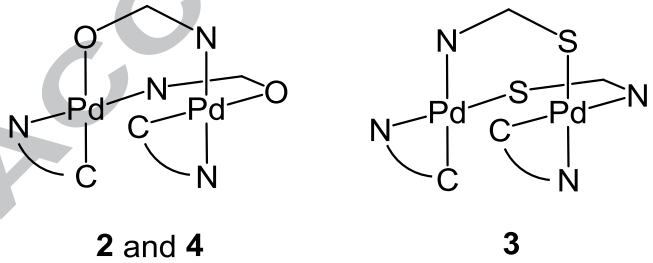

Chart 3. Ligand coordination geometries of dipalladium complexes

While gross structure features of complexes **2-4** are very similar closer inspection shows that there are some important differences. In the sac derivative **2 ,** the nitrogen atoms of the sac ligands lie *trans* to those of the metalated ligands [N1-Pd-N2 177.2(2)^o], with oxygens lying

trans to carbon [O1[a]-Pd-C9 171.7(2)°; [a]: x, -y+1/2, -z]. For the tsac complex **3**, sulphur lies *trans* to the nitrogen of the metalated ligand [N3-Pd1-S4 167.8(2)°], while the nitrogen of the tsac ligands lie *trans* to the carbon of the metalated ligand C15-Pd1-N1 174.4(2)°]. The bit complex **4** superficially closely resembles the structure of the sac derivative, the nitrogens all lie *trans* to one another [N1-Pd1-N3 175.7(2)°], while oxygens lie *trans* to the carbons of the metalated ligands [O2-Pd1-C15 172.3(2)°]. In the related N-S bonded pyridine-2-thionate complex [Pd($Me_2NCH_2C_6H_4$-κ^2N,C)(μ-SC_5H_4N)]$_2$ [**31**] the sulfurs also lie *trans* to the nitrogens of the metalated ligands [N-Pd-S 166.8(2) and 167.6(2)°] [**43**]. In all three structures Pd-C and Pd-N bond lengths to the metalated ligands of 1.963(7)-1.993(7) and 2.075(5)-2.119(5) Å respectively are within the expected ranges. The palladium-nitrogen bond lengths to the introduced ligands cover a wider range; those in **2** [2.056(6) Å] and **4** [2.062(5) Å], being significantly shorter than that in **3** [2.162(6) Å] being related to the nature of the *trans* ligand. For comparison, Pd-N and Pd-S bond lengths to the pyridine-2-thionate ligands in [Pd($Me_2NCH_2C_6H_4$-κ^2N,C)(μ-SC_5H_4N)]$_2$ of 2.157(7)-2.184(7) and 2.295(2)-2.305(2) Å respectively, are much longer [**43**]. An interesting feature of **2-4** is the relative arrangement of the two square planar Pd(II) centers. Thus in **3** and **4** they come into relatively close contact as shown by Pd···Pd distances of 3.0629(7) and 3.0281(8) Å respectively, while in **2** they are much farther apart [Pd···Pd 3.5148(1) Å]. A similar observation is made between the pyridine-2-thionate complex [Pd($Me_2NCH_2C_6H_4$-κ^2N,C)(μ-SC_5H_4N)]$_2$ and its selenium analogue [**43**] which are characterised by Pd···Pd distances of 2.976(2) and 3.420 Å respectively. Closely related to **2-4** are [Pd($Me_2NCH_2C_6H_4$-κ^2N,C)(μ-O_2CCF_3)]$_2$ [**29**] and [Pd($Me_2NCH_2C_6H_4$-κ^2N,C)(μ-HNCPhO)]$_2$ [**30**] which are characterised by Pd···Pd interactions of 3.0588(4) and 3.005(1) Å respectively. The N,O-bridge in [Pd($Me_2NCH_2C_6H_4$-κ^2N,C)(μ-HNCPhO)]$_2$ [**30**] closely resembles that in **2** yet in the latter the Pd···Pd interactions is ca. 0.5 Å longer. This is a non-bonding interaction and thus is likely to be highly dependent upon the steric and electronic properties of the associated ligands. In the homoleptic pyridine-2-thionate complex [Pd_2(μ-$SC_5H_4N)_4$] a very short Pd···Pd distance of 2.677(1) Å is noted [**47**] being significantly shorter (as are those in **3-4**) than the sum of the van der Waals radii for two palladium atoms of 3.26 Å [**48**]. The elongation of the Pd···Pd interaction in **2** appears to result from a significant twisting of the two square planar PdN_2OC centers with respect to one another as shown by the torsional angles of 26.8 and 39.9° between the two sac ligands. These contrast with related torsional angles of 10.4 and 13.8° in

4 and 19.6 and 20.7° in **3**. It is not exactly clear how these affect the Pd···Pd interaction but it is obvious that there is a good degree of flexibility between the two PdN_2CX centers.

Spectroscopic data for **2-4** suggest that the solid state structures are maintained in solution. In all cases only a single isomer is noted and we make the assumption that this is that observed in the solid state. In the ^{1}H NMR spectra the twelve methyl protons are always observed as a (slightly broad) singlet. From the solid state structures it is clear that there are two methyl environments and thus two signals would be expected. Deeming and co-workers have previously noted this for the 6-methyl pyridine-2-thionate complex $[Pd(Me_2NCH_2C_6H_4$-$\kappa^2N,C)(\mu$-$SC_5H_3MeN)]_2$ [**31**]. Upon cooling they found that the broad singlet split into two signals of equal intensity and attributed the observed changes to an intramolecular fluxional process suggested to be (but not proven) cleavage of a Pd-N bond to the 6-methyl pyridine-2-thionate ligand followed by rotation about the remaining Pd-S bond and reformation. We thus suggest similar processes must operate in **2-4**, that is cleavage of a Pd-N bond to one of the bridging ligands followed by rapid rotation about the remaining Pd-O or Pd-S bond.

3.2. Synthesis and characterisation of mono-substituted $[Pd(Me_2NCH_2C_6H_4$-$\kappa^2N,C)(\mu$-$X)]_2$ (X = sac, tsac)

Reactions of $[Pd(Me_2NCH_2C_6H_4$-$\kappa^2N,C)(\mu$-$Cl)]_2$ with simple thiolate ligands generally result in substitution of only a single bridging halide to give products of the type $[Pd_2(Me_2NCH_2C_6H_4$-$\kappa^2N,C)_2(\mu$-$Cl)(\mu$-thiolate)] resulting [**49**], while other monosubsituted derivatives such as $[Pd_2(Me_2NCH_2C_6H_4$-$\kappa^2N,C)_2(\mu$-$Cl)(\mu$-$PPh_2)]$ have also been prepared [**50**,**51**]. From reactions of one equivalent of Nabit with $[Pd(Me_2NCH_2C_6H_4$-$\kappa^2N,C)(\mu$-$Cl)]_2$ we were only able to isolate the disubstituted complex **4**, however, with both one equivalent of Nasac and tsacH different products resulted which have been characterised by analytical and spectroscopic data as the monosubsituted $[Pd_2(Me_2NCH_2C_6H_4$-$\kappa^2N,C)_2(\mu$-$Cl)(\mu$-sac)] (**5**) and $[Pd_2(Me_2NCH_2C_6H_4$-$\kappa^2N,C)_2(\mu$-$Cl)(\mu$-tsac)] (**6**) respectively. Most informative are the ^{1}H NMR spectrum which clearly show a sac/tsac to metalated ligand ratio of 1:2 together with formation of a single isomer. Somewhat unexpectedly, all four methyl groups are equivalent. This would not be expected if the added ligand bound in a μ-N-E fashion as found in **2-3** since this would clearly render the two palladium centers inequivalent. Thus either the complexes are highly fluxional (although it is not easy to see how this could interconvert the

palladium atoms) or the sac-tsac ligands are bound in a monodentate bridging manner through either the nitrogen or oxygen or sulfur. We favour the latter as we have recently prepared a number of cadmium-tsac complexes in which the tsac ligands spans two cadmium centers through binding only via sulfur [**52**]. In this respect then the tsac complex **6** could then be considered as a simple thiolate derivative of the type $[Pd_2(Me_2NCH_2C_6H_4\text{-}\kappa^2N,C)_2(\mu\text{-}Cl)(\mu\text{-thiolate})]$ [**49**]. On this basis we might then suggest that in **5** the sac ligand binds only through oxygen as a functionalised alkoxide ligand [**1**]. While as far as we are aware such alkoxide species have not been isolated, the related hydroxide complexes $[Pd_2(Me_2NCH_2C_6H_4\text{-}\kappa^2N,C)_2(\mu\text{-}X)(\mu\text{-}OH)]$ (X = Cl, Br) have both been prepared and crystallographically characterised [**53,54**]. The O-sac and S-tsac binding in **5** and **6** respectively may also account for their quite different colour; off-white and brown. Unfortunately we have been unable to confirm this by crystallography.

3.3. Synthesis and characterisation of [Pd(Me$_2$NCH$_2$C$_6$H$_4$-κ^{2}N,C)Cl(ampyH-κ^{1}N)]

After successfully preparing sac, tsac and bit complexes **2-6** we considered preparing a related 2-amino-3-methylpyridine (ampyH) complex $[Pd(Me_2NCH_2C_6H_4\text{-}\kappa^2N,C)(\mu\text{-ampy})]_2$ from reaction of **1** and two equivalents of ampyH in the presence of NEt_3 with the expectation that elimination of HCl might result. However, this reaction rather than giving the target product instead afforded mononuclear $[Pd(\text{-}\kappa^2N,CMe_2NCH_2C_6H_4)Cl(ampyH\text{-}\kappa^1N)]$ (**7**) as a pale yellow solid in 91% yield. Characterisation was straightforward based on analytical and spectroscopic data and also from an X-ray crystallographic study the results of which are summarised in Figure 4 and its caption. The structure confirms the so-called "bridge-splitting" of **1** and the overall coordination geometry is very similar to related Pd(II) complexes containing 2-aminopyridine (2-apyH) and 2-aminopyrimidine (2-apymH) and a metalated 2-pyridine ligand [**55**]. In all these complexes the two nitrogen atoms lie *trans* to one another [**7** N1-Pd1-N2 174.0(1)^o] and the Pd-N bond to the ampyH ligand [Pd1-N2 2.047(2) Å] is slightly shorter than that to the dimethylamine group [Pd1-N1 2.084(2) Å]. The arene ring of the ampyH ligand lies approximately perpendicular to the $PdClCN_2$ plane as found in related complexes. The solid state structure is maintained in solution, a virtual triplet consisting of two overlapping doublets being observed at for the NMe_2 groups at 2.76 ppm. Clearly loss of HCl has not occurred and this most likely requires a stronger base than

NEt_3. Thus, reaction of **1** with ampyH closely follows that of pyridine which has been reported to yield [Pd($Me_2NCH_2C_6H_4$-κ^2N,C)Cl(py)] [**32, 37, 56, 57**].

4. Summary and Conclusions

In this work we have compared reactions of the closely related amide ligands saccharinate, thiosaccharinate and benzisothiozolinate with the widely studied dipalladium complex [Pd($Me_2NCH_2C_6H_4$-κ^2N,C)(μ-Cl)]$_2$. For each, stepwise substitution of the bridging halides is observed leading sequentially to [Pd_2($Me_2NCH_2C_6H_4$-κ^2N,C)$_2$(μ-Cl)(μ-X)] (X = sac, tsac) and [Pd($Me_2NCH_2C_6H_4$-κ^2N,C)(μ-X)]$_2$ (X = sac, tsac, bit). The molecular structures of all disubstituted complexes reveal that the introduced amide ligands bridge the dipalladium centre adopting a relative *cis* conformation. While the gross structures are similar, small but potentially significant changes in the conformation about each palladium is noted upon changing the added ligand type. The sac and bit complexes are similar in that nitrogen atoms lie *trans* to one another, while in the tsac complex they are *cis*. The complexes differ significantly in the nature of the non-bonding Pd···Pd interaction, which is around 3 Å for the tsac and bit complexes but over 0.5 Å longer in the sac complex. This shows that this ligand framework is extremely flexible. Reaction of dimeric [Pd($Me_2NCH_2C_6H_4$-κ^2N,C)(μ-Cl)]$_2$ with 2-amino-3-methylpyridine in the presence of base affords [PdCl($Me_2NCH_2C_6H_4$-κ^2N,C)(ampyH-κ^1N)] as a result of "bridge-splitting", the ampyH ligand binding through the pyridyl-nitrogen and lying approximately perpendicular to the $PdCClN_2$ plane.

Acknowledgements

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Appendix A Supplementary data

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, 1518322 for **2**, 1518323 for **3,** 1518324 for **4** and 1815801 for **7**. Copies of this information may be obtained free of charge from the Director, CCDC, 12

Union Road, Cambridge, CB2 1 EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.ac.uk).

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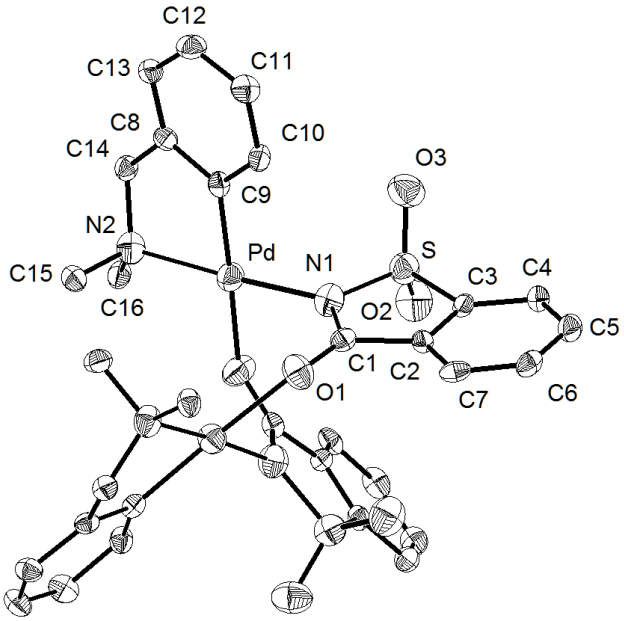


Figure 1. The molecular structure of [Pd($Me_2NCH_2C_6H_4$-κ^2N,C)(μ-sac)]$_2$ (**2**) with selected bond lengths (Å) and angles (°), thermal ellipsoids at the 50% level, hydrogen atoms omitted for clarity: Pd···Pd 3.515(6), Pd-C9 1.967(7), Pd-N1 2.056(6), Pd-N2 2.075(5), Pd-O1#1 2.180(5), C9-Pd-N1 94.9(2), C9-Pd-N2 82.5(2), C9-Pd-O1#1 171.2(2), N1-Pd-N2 177.2(2), N1-Pd-O1#1 90.6(2), N2-Pd-O1#1 91.9(2).

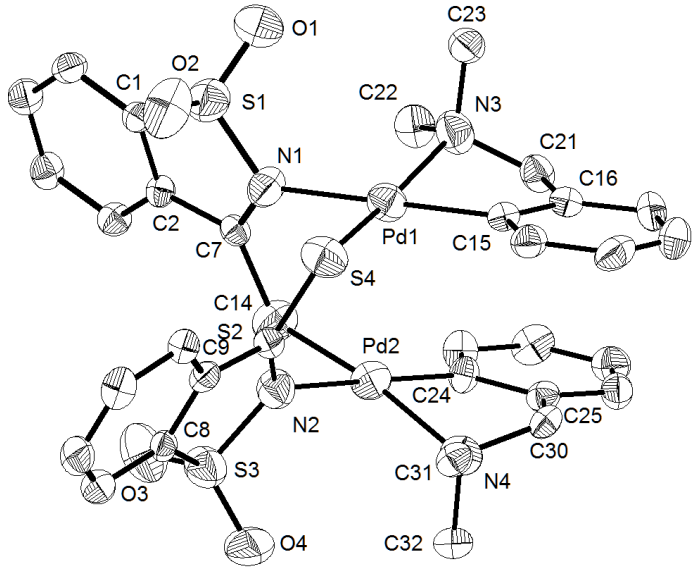


Figure 2. The molecular structure of [Pd($Me_2NCH_2C_6H_4$-κ^2N,C)(μ-tsac)]$_2$ (**3**) with selected bond lengths (Å) and angles (°) , thermal ellipsoids at the 50% level, hydrogen atoms omitted for clarity: Pd1-Pd(2) 3.0629(7), Pd1–C15 1.982(7), Pd1–N1 2.162(6), Pd1–N3 2.113(5), Pd1-S4 2.296(2), C15-Pd1-N3 81.0(2), C15-Pd1-N1 174.4(2), N3-Pd1-N1 94.2(2), C(15)-Pd1-S4 93.4(2), N3-Pd1-S4 167.8(2), N1-Pd1-S4 91.9(1).

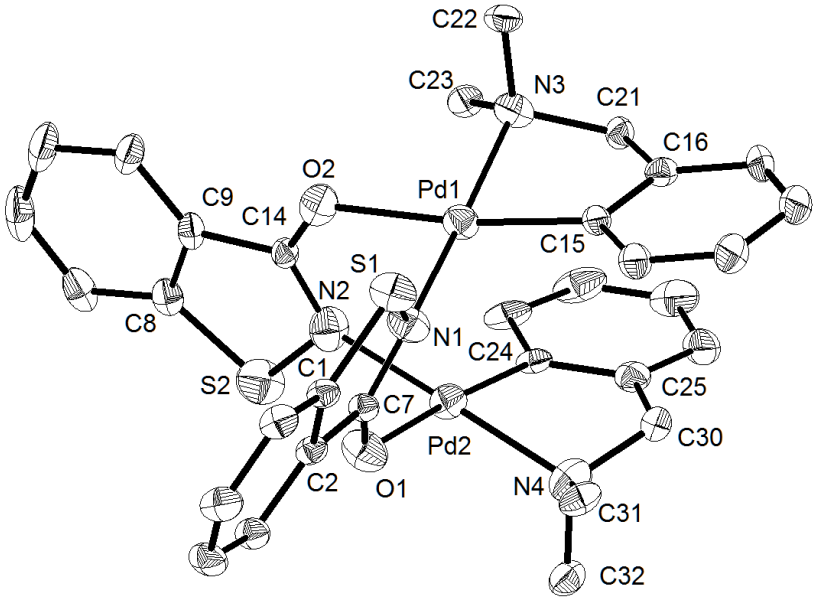


Figure 3. The molecular structure of [Pd($Me_2NCH_2C_6H_4$-κ^2N,C)(μ-bit)]$_2$ (**4**) with selected bond lengths (Å) and angles (°) , thermal ellipsoids at the 50% level, hydrogen atoms omitted for clarity: Pd1-Pd2 3.0281(8), Pd1-C15 1.980(7), Pd1-N1 2.062(5), Pd1-N3 2.092(6), Pd1-O2 2.147(5), C15-Pd1-N1 96.9(3), C15-Pd1-N3 82.1(3), N1-Pd1-N3 175.7(2), C15-Pd1-O2 172.3(2), N1-Pd1-O2 90.22, N3-Pd1-O2 90.6(2).

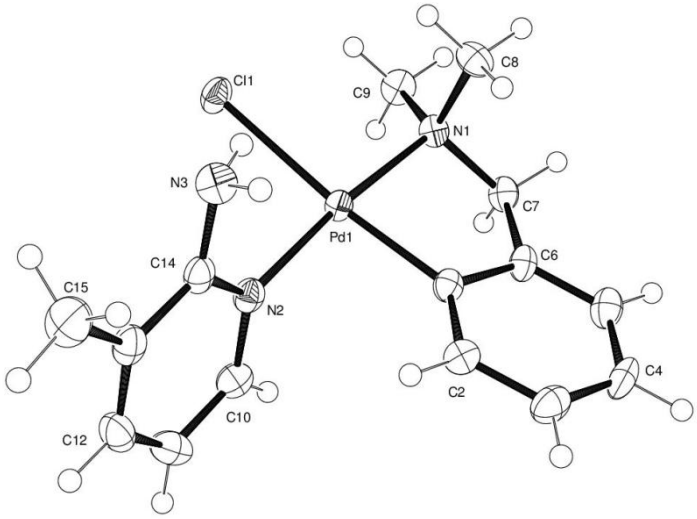


Figure 4. The molecular structure of [Pd($Me_2NCH_2C_6H_4$-κ^2N,C)Cl(ampy-κ^1N)] **(7)** with selected bond lengths (Å) and angles (°): Pd1-Cl1 2.4360(7), Pd1-N1 2.084(2), Pd1-N2 2.047(2), Pd1-C1 1.979(3), N1-Pd1-Cl1 94.49(7), N2-Pd1-Cl1 91.34(7), N2-Pd1-N1 174.04(10), C1-Pd1-Cl1 173.36(8), C1-Pd1-N2 91.89(11).

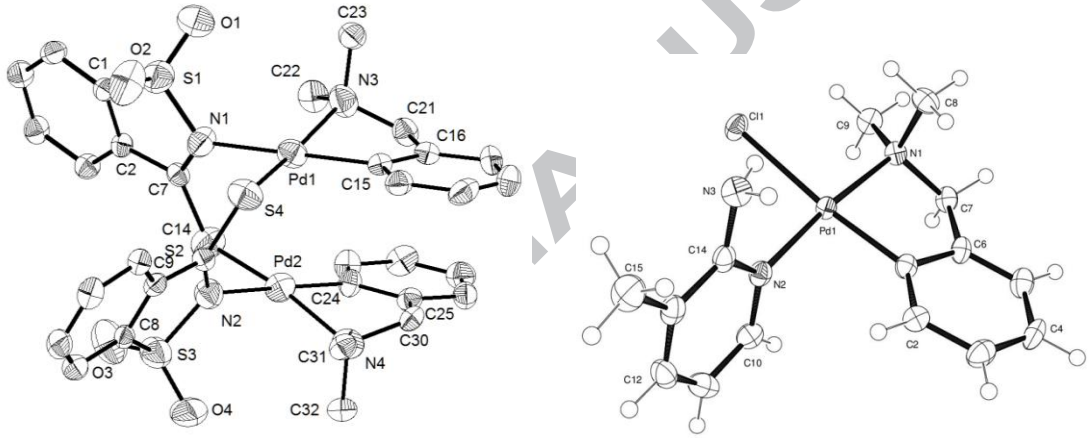
Table 1. Crystallographic data

Compound	**2**	**3·DMF**	**4·$CHCl_3$**	**7**
Empirical formula	$C_{32}H_{32}N_4O_6Pd_2S_2$	$C_{35}H_{39}N_5O_5Pd_2S_4$	$C_{33}H_{33}Cl_3N_4O_2Pd_2S_2$	$C_{15}H_{20}ClN_3Pd$
Formula weight	805.28	950.75	900.90	384.21
Temperature (K)	200(2)	293(2)	200(2)	150 (2)
Crystal system, space group	orthorhombic, Pbna	monoclinic $P2_1/c$	orthorhombic $Pc2_1n$	monoclinic $P2_1/c$
Unit cell dimensions				
a (Å)	9.1353(4)	10.5465(8)	14.2439(3)	14.6918(3)
b (Å)	18.0446(7)	32.192(3)	14.7164(3)	9.9499(2)
c (Å)	19.202(1)	12.2367(9)	16.7691(5)	11.0931(2)
α (°)	90	90	90	90
β (°)	90	114.877(5)	90	104.701(2)
γ (°)	90	90	90	90
Volume (A^3)	3165.3(2)	3769.1(5)	3515.1(2)	1568.52(6)
Z	8	4	4	4
Density (calc.) (g/cm^3)	1.774	1.675	1.702	1.6269
Absorption coefficient (mm^{-1})	1.320	1.224	1.407	1.347
F(000)	2176	1920	1800	772.8
Crystal size (mm)	0.10 x 0.10 x 0.10	0.42 x 0.34 x 0.14	0.48 x 0.25 x 0.22	0.24 × 0.23 × 0.16
Theta range for data collection (^{o})	2.12 to 25.00	3.81 to 25.00	1.88 to 25.00	3.52 to 29.7
Limiting indices	-10<=h<=10, -21<=k<=21, -22<=l<=22	-11<=h<=12, -38<=k<=33, -14<=l<=14	-16<=h<=16, -15<=k<=17, -19<=l<=19	-18 ≤ h ≤ 15, -10 ≤ k ≤ 12, -8 ≤ l ≤ 13
Reflections collected/ Independent reflection	19118 / 2792	16142/ 6591	21894 / 5551	10843/3660
[Rint]	0.1677	0.1023	0.0679	0.0397
Completeness to θ = 25.00	100 %	99.2 %	99.6 %	94.5 %
Max./min. transmission	0.9514 / 0.7884	0.8672 / 0.7075	0.7472 / 0.5516	0.843 /0.785
Data / restraints / parameters	2792 / 0 / 208	6591 / 0 / 469	5551 / 1 / 416	3660/0/184
Goodness-of-fit on F2	1.015	0.800	1.033	1.041
Final R indices [I>2σ(I)]	R1 = 0.0477, wR2 = 0.0709	R1 = 0.0404, wR2 = 0.0816	R1 = 0.0328, wR2 = 0.0875	R1 = 0.0327, wR2 = 0.0774
R indices (all data)	R1 = 0.1007, wR2 = 0.0869	R1 = 0.0892, wR2 = 0.1106	R1 = 0.0339, wR2 = 0.0886	R1 = 0.0402, wR2 = 0.0834
Largest diff. peak/hole ($e \cdot Å^{-3}$)	0.657/-0.452	0.615/-1.248	1.584/-1.299	0.92 -0.84

Graphical abstract

Graphic abstract

Reactions of $[Pd(\kappa^2\text{-}Me_2NCH_2C_6H_4)(\mu\text{-}Cl)]_2$ with two equivalents of sodium saccharinate (Nasac), thiosaccharin (Htsac) or sodium benzisothiozolinate (Nabit) results in stepwise chloride substitution to afford $[Pd(\kappa^2\text{-}Me_2NCH_2C_6H_4)(\mu\text{-}X)]_2$ (X = sac, tsac, bit), while with 2-amino-3-methylpyridine (ampyH) in the presence of NEt_3 mononuclear $[PdCl(\kappa^2\text{-}Me_2NCH_2C_6H_4)(\kappa^1\text{-}ampyH)]$ results.



Highlights

- Synthesis of dipalladium complexes with bridging sac, tsac and bit ligands
- Crystal structures of three examples showing subtle differences in conformation
- Formation of mononuclear complex resulting from bridge cleavage upon addition of 2-amino-3-methylpyridine