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Palladium(II) saccharinate complexes *trans*-$[Pd(sac)_2(LH)_2]$ with amino- and acetylamino-pyridine co-ligands: molecular structures of *trans*-$[PdCl_2(2\text{-ampyH})_2]$.2dmf (2-ampyH = 2-amino-3-methylpyridine) and *trans*-$[Pd(\kappa^2\text{-}2\text{-acmpy})_2]$ (2-acmpyH = 2-acetylamino-3-methylpyridine)

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Abstract Reaction of $Na_2[PdCl_4]$ with two equivalents of amino- or acetylamino-pyridines (LH) affords *trans*-$[PdCl_2(LH)_2]$ {LH = 2-amino-3-methylpyridine (2-ampyH), 3-aminopyridine (3-apyH), 2-acetylamino-3-methylpyridine (2-acmpyH), 3-acetylamino-pyridine (3-acpyH)}. An X-ray crystal structure of *trans*-$[PdCl_2(2\text{-ampyH})_2]$ shows that the 2-ampy-H ligands are coordinated in a monodentate fashion via the nitrogen atoms of the pyridine rings. Treatment of *trans*-$[PdCl_2(2\text{-acmpyH})_2]$ with NEt_3 affords the cyclometalated complex, *trans*-$[Pd(\kappa^2\text{-}2\text{-acmpy})_2]$, the X-ray structure of which shows that the 2-acmpy ligand is coordinated to palladium in a bidentate fashion via the nitrogen atom of the pyridine ring and oxygen. Reaction of *trans*-$[PdCl_2(LH)_2]$ with two equivalents of sodium saccharinate affords the bis(saccharinate) complexes, *trans*-$[Pd(sac)_2(LH)_2]$, in which the saccharinate anions are coordinated via the amide nitrogen atom.

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Introduction

There is continued interest in the chemistry of saccharinate (sac) complexes as co-ligands in biological studies [1, 2], and consequently, a number of reports have recently appeared on the synthesis of platinum and palladium saccharinate complexes [3–11]. While saccharinate can bind to metal centres in a variety of different ways [1, 2] at the relatively *soft* Pd(II) and Pt(II) centres, it is always N-bound (Fig. 1). Thus, the inclusion of other N-bound ligands to these metal centres results in the formation of an MN_4 coordination sphere. Continuing our recent studies in this area [12–14], we herein provide details of the synthesis of four new palladium saccharinate complexes, *trans*-$[Pd(sac)_2(LH)_2]$, derived from commercially available or readily prepared amino- or acetylamino-pyridines. Yilmaz and co-workers have also recently detailed the synthesis of related complexes with pyridine and substituted pyridine co-ligands [6–11] and have studied their biological properties [16–19].

Experimental

Materials and methods

All reactions were carried out in the open air using standard bench reagents. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on Varian Unity 500 and Gemini 2000 spectrometers, respectively, with $CDCl_3$, d^6-dmso or d^7-dmf as solvent and internal reference. IR spectra were recorded on a Shimadzu FT-IR 8400 spectrophotometer in the 400–4,000 cm^{-1} range using KBr discs and in the 200–600 cm^{-1} using CsI discs.

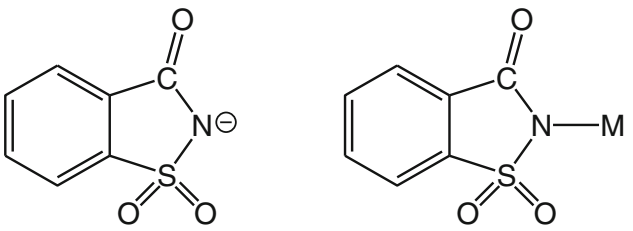


Fig. 1 Saccharinate (sac) and its most common metal binding mode

Elemental analyses were carried out at Martin-Luther-Universität. Melting points were measured on a Gallenkhamp melting point apparatus and are uncorrected. $Na_2[PdCl_4]$, 3-aminopyridine and 2-amino-3-methylpyrimidine were purchased and used as supplied. 3-Acetylamino-pyridine (3-acpyH) [20] and 2-acetylamino-3-methylpyridine (2-acmpyH) [21] were prepared by literature methods. The latter was recrystallized from benzene/hexane (ca 1:1) and characterized prior to use. 2-acmpyH: White prisms, 91 %. Anal Calc. for $C_8H_{10}N_2O$: C, 64.0; H, 6.7; N, 18.7. Found: C, 64.0; H, 6.6; N, 18.8; IR (KBr): 3236 s, 3028w, 2956w, 1666 s, 1527 s cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.22 (dd, 1H, py), $^3J(HH) = 6.0$ Hz, $^4J(HH) = 1.2$ Hz, 7.6 (d, 1H, py), $^3J(HH) = 7.5$ Hz, 7.12 (dd, 1H, py), $^3J(HH) = 7.5$ Hz, 2.28 (s, 3H, CH_3), 2.32 (s, 3H, CH_3) ppm. Melting point: 52 °C.

Synthesis of **1a–d**

A solution of 2-amino-3-methylpyridine (2-ampyH) (0.11 g, 1.0 mmol) in ethanol (10 cm^3) was added to a solution of $Na_2[PdCl_4]$ (0.15 g, 0.50 mmol) in ethanol (10 cm^3). The mixture was stirred at room temperature for 3 h. The yellow solid thus formed was filtered off, washed with water and ethanol, and dried under vacuum to give *trans*-$[PdCl_2(2\text{-ampyH})_2]$ (**1a**) (0.16 g, 93 % yield). The related complexes *trans*-$[PdCl_2(3\text{-apyH})_2]$ (**1b**), *trans*-$[PdCl_2(2\text{-acmpyH})_2]$ (**1c**) and *trans*-$[PdCl_2(3\text{-acpyH})_2]$ (**1d**) were prepared and isolated in a similar manner. Crystals of **1a**.2dmf suitable for single-crystal diffraction analysis were grown at 25 °C upon standing a dmf solution for several days. **1a**: Yellow solid, 93 %. Anal Calc. for $C_{12}H_{16}Cl_2N_4Pd$: C, 32.2; H, 4.9; N, 12.5. Found: C, 32.2; H, 4.8; N, 12.3 %; IR (KBr) : 3340 s, 3334 s, 2950w, 1620 s, 1479 s, 1271 m, 1200 m, 751 m, 513 m, 338 m cm^{-1}. ^1H NMR (d^7-dmf): δ 8.52 (d, 1H, py), 7.55 (d, 1H, py), 7.28 (s, 2H, NH_2), 6.73 (t, 1H, py), 2.34 (s, 3H, CH_3) ppm, $^3J(HH) = 5.7$–7.0 Hz. **1b**: Yellow solid, 88 %. Anal Calc. for $C_{10}H_{12}Cl_2N_4Pd$: C, 32.8; H, 3.3; N, 15.3. Found: C, 33.1; H, 3.2; N, 15.6 %; IR (KBr): 3445 s, 3337 s, 3020w, 1627 s, 1596 s, 1568 m, 1498 s, 758 m, 461w, 347 s cm^{-1}. ^1H NMR (d^6-dmso): δ 8.33 (d, 1H, py), 7.43 (t, 1H, py), 7.32 (s, 2H, NH_2), 6.57 (d, 1H, py), 6.44 (t, 1H, py) ppm, $^3J(HH) = 8.4$ Hz, $^4J(HH) = 5.6$ Hz. **1c**: Pale yellow solid, 91 %. Anal Calc. for $C_{16}H_{20}Cl_2N_4O_2Pd$: C, 40.1; H, 4.2; N, 11.7. Found: C, 40.5; H, 4.4; N, 12.0 %; IR (KBr): 3240 s, 3070w, 2977 m, 2927 m, 1689 s, 1596 s, 1598, 792 s, 528 m, 355 m cm^{-1}. ^1H NMR (d^7-dmf): δ 10.74 (bs, 1H, NH), 9.03 (d, 1H, py), 8.06 (d, 1H, py), 7.55 (dd, 1H, py), 2.26 (s, 3H, CH_3), 2.58 (s, 3H, CH_3) ppm, $^3J(HH) = 5.4$–7.4 Hz. **1d**: Yellow solid, 89 %. Anal Calc. for $C_{14}H_{16}Cl_2N_4O_2Pd$: C, 37.4; H, 3.6; N, 12.5. Found: C, 37.6; H, 3.7; N, 12.7 %; IR (KBr): 3317 s, 3060w, 2877 m, 1701 s, 1578 m, 773 s, 513 m, 364 m cm^{-1}. ^1H NMR (d^6-dmso): δ 10.4 (s, 1H, NH), 8.28 (d, 1H, py), 8.04 (d, 1H, py), 7.74 (t, 1H, py), 7.06 (t, 1H, py), 2.08 (s, 3H, CH_3) ppm, $^3J(HH) = 8.2$ Hz, $^4J(HH) = 3.7$ Hz.

Synthesis of **2**

Several drops of NEt_3 were added to a suspension of *trans*-$[PdCl_2(2\text{-acmpyH})_2]$ (**1c**) (0.20 g, 0.44 mmol) in ethanol (10 cm^3). The mixture was stirred at room temperature for 3 h. The pale yellow solid was filtered off, washed with ethanol and dried in a vacuum oven (0.12 g, 60 %). Crystals of **2** suitable for single-crystal diffraction analysis were grown by the slow evaporation of a saturated $CHCl_3$ solution. **2**: Pale green-yellow solid, 60 %. Anal Calc. for $C_{16}H_{18}N_4O_2Pd$: C, 48.8; H, 4.8; N, 13.8. Found: C, 48.5; H, 5.0; N, 14.0 %; IR (KBr): 3097w, 2958w, 1579 s, 767 m, 505w cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.26 (dd, 1H, py), 7.44 (dd, 1H, py), 6.72 (dd, 1H, py), 2.29 (s, 3H, CH_3), 2.16 (s, 3H, CH_3) ppm, $^3J(HH) = 6.1$–7.1 Hz, $^4J(HH) = 0.8$–1.2 Hz. Melting point: 206–208 °C.

Synthesis of **3a–d**

A solution of sodium saccharinate (0.10 g, 0.50 mmol) in ethanol (10 cm^3) was added to a suspension of *trans*-$[PdCl_2(2\text{-ampyH})_2]$ (**1a**) (0.10 g, 0.25 mmol) in ethanol (7 cm^3). The mixture was stirred for 4 h. The cream-coloured precipitate was filtered off, washed with water and ethanol, then dried under vacuum (0.098 g, 98 % yield). The complexes *trans*-$[Pd(sac)_2(3\text{-apyH})_2]$ (**3b**), *trans*-$[Pd(sac)_2(2\text{-acmpyH})_2]$ (**3c**) and *trans*-$[Pd(sac)_2(3\text{-acpyH})_2]$ (**3d**) were prepared and isolated in a similar manner. **3a**: Pale yellow solid, 98 %. Anal Calc. for $C_{26}H_{24}N_6O_6PdS_2$: C, 45.5; H, 3.5; N, 12.2. Found: C, 45.8; H, 3.7; N, 12.4 %; IR (KBr): 3438 s, 3344 s, 3083w, 2955w, 1652 s, 1596 m, 1307 s, 1257 s, 1166 s, 530w cm^{-1}. ^1H NMR (d^6-dmso): δ 8.31 (s, 1H, py), 7.83–7.65 (m, 6H, NH_2, sac), 7.1 (d, 1H, py), 6.5 (d, 1H, py), 1.98 (s, 3H, CH_3). **3b**: Pale yellow solid, 91 %. Anal Calc. for $C_{24}H_{18}N_4O_6PdS_2$: C, 43.7; H, 3.1; N, 12.8. Found: C, 43.8; H, 3.30; N, 13.0 %; IR (KBr): 3427 s, 3311 m, 3209 m, 3088w, 1666 s, 1635 s, 1601 s, 1452, 1254 s, 1163 s,

Table 1 Crystallographic data and structure refinement details for **1**.2dmf and **2**

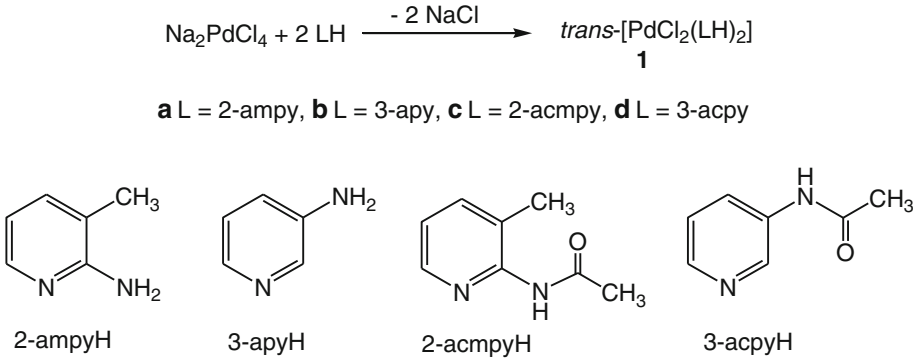
Compound	**1**.2dmf	**2**
Empirical formula	$C_{18}H_{30}Cl_2N_6O_2Pd$	$C_{16}H_{18}N_4O_2Pd$
Formula weight (Å)	539.78	404.74
Temperature (K)	200(2)	220(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$I2/a$
Unit cell dimensions		
a (Å)	7.3933(7)	14.126(1)
b (Å)	11.1888(7)	7.4669(9)
c (Å)	14.022(1)	14.809(1)
α (°)	90	90
β (°)	90.639(12)	95.57(1)
γ (°)	90	90
Volume (Å^3)	1,159.9(2)	1,554.7(3)
Z	2	4
Density (calculated) (Mg/m^3)	1.546	1.729
Absorption coefficient (mm^{-1})	1.056	1.209
F(000)	552	816
Crystal size (mm)	0.44 × 0.32 × 0.20	0.38 × 0.22 × 0.07
θ Range for data collection (°)	2.33–26.00	3.06–25.96
Index ranges	$-9 \leq h \geq 9$	$-17 \leq h \geq 17$
	$-13 \leq k \geq 12$	$-9 \leq k \geq 9$
	$-17 \leq l \geq 17$	$-18 \leq l \geq 17$
Reflections collected	8,114	5,787
Independent reflections [R_{int}]	2,258 [$R_{int} = 0.0294$]	1,474 [$R_{int} = 0.0547$]
Data/restraints/parameters	2,258/0/133	14,749/0/107
Goodness-of-fit on F^2	1.107	1.026
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0280$,	$R_1 = 0.0286$,
	$wR_2 = 0.0736$	$wR_2 = 0.0740$
R indices (all data)	$R_1 = 0.0345$,	$R_1 = 0.0373$,
	$wR_2 = 0.0757$	$wR_2 = 0.0777$
Largest diff. peak and hole (e.Å^{-3})	0.547 and −0.714	0.510 and −0.503

761 s, 530 s cm^{-1}. ^{1}H NMR (d^6-dmso): δ 8.33 (d, 1H, py), 7.86–7.58 (m, 4H, sac), 7.41 (t, 1H, py), 7.27 (s, 2H, NH_2), 6.59 (d, 1H, py), 6.50 (t, 1H, py) ppm, ^3J(HH) = 8.0 Hz. **3c**: White solid, 80 %. Anal Calc. for $C_{30}H_{28}N_6O_8PdS_2$: C, 47.3; H, 4.7; N, 9.9. Found: C, 47.1; H, 4.9; N, 10.0 %; IR (KBr): 3240w, 3188w, 2968w, 1703 s, 1652 s, 1595 s, 1251 s, 1164 s, 756 m, 522 m cm^{-1}. ^{1}H NMR (d^6-dmso): δ 9.94 (s, 1H, NH), 8.24 (d, 1H, py), 8.05 (d, 1H, sac), 7.87–7.70 (m, 3H, sac), 7.65 (d, 1H, py), 7.18 (dd, 1H, py), 2.14 (s, 3H, CH_3), 2.03(s, 3H, CH_3) ppm, ^3J(HH) = 8.0 Hz. **3d**: Pale yellow, 92 %. Anal Calc. for $C_{28}H_{24}N_6O_8PdS_2$: C, 45.3; H, 3.3; N, 11.3. Found: C, 45.6; H, 3.4; N, 11.4 %; IR (KBr): 3263 s, 3215w, 3080w, 1714 s, 1655 s, 1581 m, 1437 s, 1254 s, 1165, 761 m, 517 m cm^{-1}. ^{1}H NMR (d^6-dmso): δ 10.4 (bs, 1H, NH), 8.29–7.07 (m, 8H, py and sac), 2.10 (s, 3H, CH_3) ppm.

X-ray structure determinations

Crystallographic data for **1**.2dmf and **2** were collected at 200(2) and 220(2) K, respectively, on a STOE-IPDS diffractometer with Mo-Kα radiation (λ = 0.7103 Å, graphite monochromator). Absorption corrections were made using the IPDS software package [22]. All structures were solved by direct methods with SHELX-97 [23] and refined using full-matrix least-square routines against F^2 with SHELXL-97 [24]. 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. Details of crystallographic data, collection parameters and structure refinement are summarized in Table 1.

Scheme 1 Preparation of **1a–d**



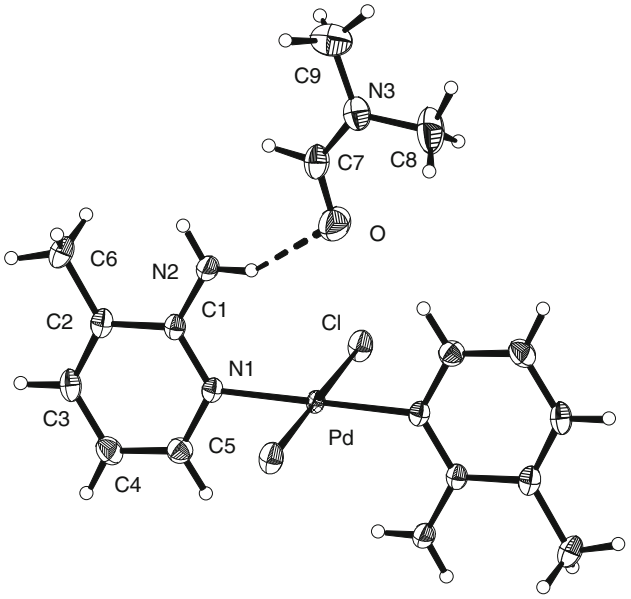


Fig. 2 The molecular structure of *trans*-[$PdCl_2$(2-ampyH)$_2$] (**1a**).2dmf with selected bond lengths (Å) and angles (°); Pd(1)–Cl(1) 2.313(1), Pd(1)–Cl(2) 2.279(1), Pd(1)–N(1) 2.016(3), Pd(1)–N(2) 2.023(3), C(1)–N(1) 1.319(5), C(1)–N(3) 1.320(6), C(8)–N(2) 1.307(6), C(8)–N(4) 1.333(6), Cl(1)–Pd(1)–Cl(2) 177.94(4), N(1)–Pd(1)–N(2) 177.6(1), Cl(1)–Pd(1)–N(1) 90.72(9), Cl(2)–Pd(1)–N(1) 88.79(9)

Results and discussion

Synthesis of trans-[$PdCl_2(LH)_2$] (**1a–d**) and X-ray crystal structure of trans-[$PdCl_2$(2-ampyH)$_2$] (**1a**)

In order to prepare the target bis(saccharinate) complexes, *trans*-[$Pd(sac)_2(LH)_2$] (**3**), we first coordinated a range of amino- and acetylamino-pyridines to the palladium(II) centre. Thus, treatment of $Na_2[PdCl_4]$ with two equivalents of aminopyridines or acetylamino-pyridines (LH = 2-apyH, 3-ampyH, 2-acmpyH or 3-acpyH) in EtOH afforded *trans*-[$PdCl_2(LH)_2$] (**1a–d**) in 82–93 % yield as illustrated in Scheme 1. Spectroscopic and analytical data are in full accord with the proposed formulations. In order to ascertain the precise coordination sphere, crystals of **1a.**2dmf were grown upon slow evaporation of a saturated dmf solution and the results of an X-ray crystallographic study are summarized in Fig. 2 and its caption. The structure shows the expected square-planar palladium(II) centre ligated by *trans* pairs of chloride and aminopyridine ligands, and bond lengths and angles are within the expected ranges [25, 26]. The two aminopyridine ligands are related by the inversion centre and thus adopt a relative anti-arrangement with the aryl rings lying approximately perpendicular to the $PdCl_2N_2$ plane. The amine substituents do not take part in the bonding to palladium but are in close contact with the dmf solvate [O···H8 2.258 Å] (as shown in Fig. 2), which is also weakly bound to a chloride [Cl···H9 2.712 Å].

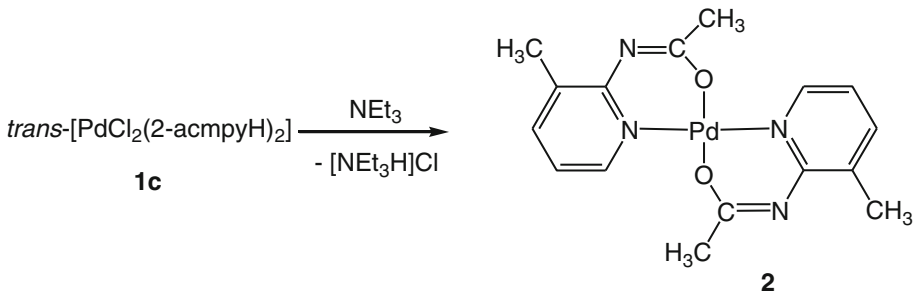
Synthesis and X-ray crystal structure of trans-[Pd(2-acmpy)$_2$] (**2**)

Addition of a few drops of NEt_3 to a suspension of *trans*-[$PdCl_2$(2-acmpyH)$_2$] (**1c**) in ethanol afforded *trans*-[Pd(2-acmpy)$_2$] (**2**) as a pale yellow solid (60 % yield) (Scheme 2). Crystals of **2** were grown upon slow evaporation of a $CHCl_3$ solution, and the results of an X-ray crystallographic study are summarized in Fig. 3 and its caption. The molecule closely resembles that of the unsubstituted derivative [27, 28] and contains a square-planar palladium(II) centre ligated by two chelating 2-acetylamino-3-methylpyridinate ligands. Palladium–nitrogen and palladium–oxygen bonds are 2.045(2) and 1.973(3) Å, respectively, and the ligand bite angle is 90.29(9)°. The bonding within each of the metallacyclic rings is localized in nature, as seen by the two different carbon–nitrogen bond distances to the nonmetal-bound nitrogen atom [C(1)–N(2) 1.375(4), C(7)–N(2) 1.304(4) Å].

Synthesis and characterization of trans-[$Pd(sac)_2(LH)_2$] (**3a–d**)

As stated in the introduction, the aim of this work was to prepare a series of bis(saccharinate) complexes containing a

Scheme 2 Preparation of **2**



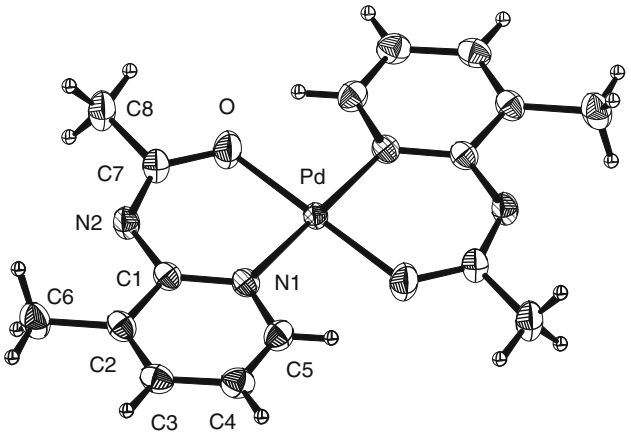
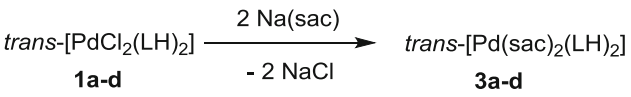


Fig. 3 The molecular structure of *trans*-[Pd(2-acmpy)$_2$] (**2**) (symmetry operation-x + 2, -y,-z) with selected bond lengths (Å) and angles (°); Pd–N(1) 2.045(2), Pd–O 1.973(3), C(1)–N(1) 1.362(4), C(5)–N(1) 1.364(4), C(1)–N(2) 1.375(4), C(7)–N(2) 1.304(4), C(7)–O 1.286(4), O–Pd–O$^{\#}$ 180, N(1) –Pd–O 90.29(9), Cl(1) –N(2) –C(7) 125.5(2), Pd–O–C(7) 125.4(2)



Scheme 3 Preparation of **3a–d**

PdN_4 core. This was readily achieved by the simple substitution of the chlorides in **1a–d**. Thus, treatment of *trans*-[$PdCl_2(LH)_2$] (**1a–d**) with two equivalents of sodium saccharinate in ethanol afforded *trans*-[$Pd(sac)_2(LH)_2$] (**3a–d**) in 80–98 % yield (Scheme 3). Characterization was straightforward, being made on the basis of analytical and spectroscopic data. The ^{1}H NMR spectra of each displayed the expected signals for the pyridine or aminopyridine ligands together with a series of multiplets between δ 7.07–8.28 corresponding to the eight protons of the saccharinate ligands. IR spectra showed strong bands within the 1,652–1,666 cm^{-1} range attributed to ν(CO) of the saccharinate anion. Unfortunately, we have been unable to grow crystals of any of these complexes suitable for single-crystal X-ray diffraction. Nevertheless, on the basis of the NMR data, we can see that a single isomer of each exists in solution. In earlier work, we [13, 15] and others [10] have noted that in some instances rotational isomers (rotamers) are seen in solution. Thus, due to steric requirements, all four nitrogen-based ligands lie perpendicular to the PdN_4 plane and these can adopt differing relative positions (*syn* or *anti*) of the substituents on sets of like ligands, leading to four possible rotamers of which only two have been observed in the solid-state [13, 15]. That adopted appears to depend upon the development of intramolecular hydrogen bonds between the two different ligand types. In the absence of crystallographic data, we cannot comment further on the isomer that is adopted for **3a–d**.

Summary and conclusions

This work has further shown that the synthesis of bis(saccharinate) complexes of the type *trans*-[$Pd(sac)_2(LH)_2$] containing amino- or acetylamino-pyridine ligands is general and straightforward starting from $Na_2[PdCl_4]$ and commercially available ligands. Further, the yields of each step are high, reactions can be carried out without the exclusion of oxygen and water and product isolation and crystallization is simple. Such complexes are known to show biological activity [16–19], while the related phosphine complex *trans*-[$Pd(PPh_3)_2(sac)_2$] has been shown to be an efficient catalyst for Suzuki–Miyaura and Negishi cross-coupling reactions [29, 30]. We are currently accessing the biological properties and catalytic properties of **3a–d** and related bis(saccharinate) complexes, the results of which will be reported in due course.

Supplementary material

CCDC 999301 and 999302 contain the supplementary crystallographic data for this article. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data-_request/cif.

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