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Palladium(II) benzisothiazolinate (bit) complexes with amino-, acetylamino-, heterocyclic and phosphine co-ligands. Crystal structure of $[Pd(bit)_2(\kappa^2\text{-dppe})].2EtOH$

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Keywords: palladium, benzisothiazolinate, phosphine, synthesis, crystal structure

ABSTRACT A series of square-planar palladium(II) benzisothiazolinate (bit) of the general type $[Pd(bit)_2L_2]$ have been prepared and characterised by analytical and spectroscopic methods. Two synthetic routes have been employed, namely reactions of $[Pd(bit)_2].H_2O$ with two equivalents of ligands (L = amine, amide, phosphine) or nucleophile displacement of chloride by benzisothiazolinate starting from *trans*-$[PdCl_2L_2]$. Both routes afford the new complexes in good yields as easily isolated, air and moisture stable, colored solids. The precursor, $[Pd(bit)_2].H_2O$, is itself prepared in high yields upon reaction of Na[bit] with $Na_2[PdCl_4]$ in methanol and the analogous platinum complex, $[Pt(bit)_2].H_2O$, is similarly prepared from $K_2[PtCl_4]$. It is not clear if these species are mono- or dimeric, and formulation as $[M_2(\mu\text{-bit})_4(H_2O)_2]$ with the four benzisothiazolinate spanning the metal-metal vector and possibly binding through coordination of nitrogen and oxygen is suggested. Diphosphine adducts, *cis*-$[Pd(bit)_2\{\kappa^2\text{-}Ph_2P(CH_2)_nPPh_2\}]$ (n = 1-4) can be prepared both upon addition of the diphosphine to $[Pd(bit)_2].H_2O$ and from reactions of *cis*-$[PdCl_2\{\kappa^2\text{-}Ph_2P(CH_2)_nPPh_2\}]$ with two equivalents of Na[bit]. A crystal structure of *cis*-$[Pd(bit)_2(\kappa^2\text{-dppe})]$ reveals that the benzisothiazolinate ligands are bonded in a monodentate fashion through nitrogen and this

binding mode is proposed for all $[Pd(bit)_2L_2]$ and $[Pd(bit)_2L]$ complexes. With dppb (n = 4) a second product is seen by NMR spectroscopy being proposed to be the part-substituted complex *cis*-$[PdCl(bit)(\kappa^2\text{-dppb})]$, while with dppm (n = 1) two further products are seen spectroscopically, proposed as *trans*-$[Pd(bit)_2(\kappa^1\text{-dppm})_2]$ and (more tenuously) $[Pd_2(bit)_4(dppm)_2]$. The former is also prepared in good yields from reaction of $[Pd(\kappa^2\text{-dppm})_2]Cl_2$ with Na[bit]. These studies show that palladium benzisothiazolinate are easily accessed and show good air and moisture stability.

Keywords: palladium, benzisothiazolinate, diphosphines, crystal structure

1. Introduction

The saccharinate anion (sac) is easily formed upon deprotonation of the acidic imine hydrogen of saccharin and has found widespread use as a versatile poly-functional ligand in the field of coordination chemistry [**1,2**]. It can adopt a variety of coordination modes being able to bind in a monodentate fashion through nitrogen or an oxygen of either the carbonyl or sulfonyl groups, while also having the capacity to bind in a bidentate or polydentate fashion through both atom types [**1**]**.** The biological properties of saccharinate complexes have attracted particular attention and we have recently reported the promising anticancer activity of the platinum(II) saccharinate complex *cis*-$[Pt(sac)_2(NH_3)_2]$ and its thiosaccarinate (tsac) analogue *cis*-$[Pt(tsac)_2(NH_3)_2]$ [**3**]. Benzoisothiazolinone (Hbit) [**4**] which is structurally similar to saccharin (Chart 1) has potent antimicrobial and anti-fungicidal properties [**5**]. The benzisothiozolinate (bit) anion results upon deprotonation of the acidic imine hydrogen and like saccharinate is potentially a versatile poly-functional ligand [**6**]. However, while saccharinate complexes of the transition [**1**] and heavy non-transition metals [**1,7-10**] are common, to our knowledge there is only a single report of a transition metal bit complex. Thus Griffith and co-workers have recently reported the synthesis of *cis*-$[Pd(bit)_2(\kappa^2\text{-en})]$ (en = ethylenediamine) and $[Pt(NH_3)_2(bit)_2]$, the former being characterized by single crystal X-ray crystallography [**11**]. Herein we report the synthesis of a number of new palladium(II)-bit complexes and show that this ligand is compatible with a range of supporting ligand types including heterocyclic amines, acetamides and phosphines.

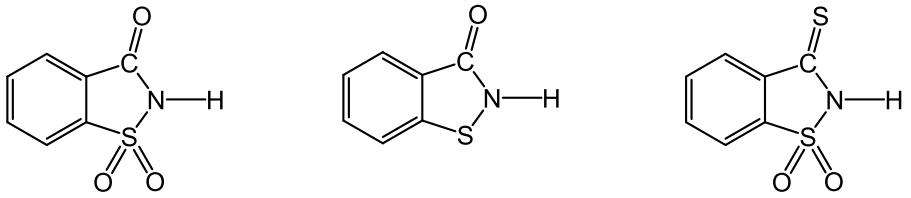


Chart 1

2. Experimental

2.1. General methods, reagents and instrumentation

^{1}H and ^{31}P{^{1}H} NMR spectra were recorded on Varian Unity and Gemini 200 spectrometers respectively with $CDCl_3$ or d^6-dmso solvent and internal reference and H_3PO_4 (85%) as external reference. IR spectra were recorded on Shimadzu FTIR 8400 spectrophotometer in the 400-4000 cm^{-1} range using KBr discs and in the 200-600 cm^{-1} using CsI discs. Elemental analyses were carried out at University College London and Al Al-Bayt University, Jorden. Melting points measured on a Gallenkamp melting point apparatus and were uncorrected. $Na_2[PdCl_4]$, benzisothiazoline (Hbit), 2-aminothiazole, 2-aminobenzothiazole (abzt), 2-aminopyridine (apy), 2-amino-3-methylpyridine (ampy), 2-aminopyrimidine, 2-amino-5-methyl-1,3,4-thiazole, 2,6-diaminopyridine (dapy) were purchased and used as supplied. Thiosaccharine (Htsac) [**12**], 2-acetylaminothiazole (actz) [**13**], 2-acetylaminobenzothiazole (acbzt) [**13**], 2-acetylamino-3-methylpyridine (acmpy) [**13**], 2-acetylaminopyrimidine (acpym) [**14**], 2-acetylamino-5-methyl-1,3,4-thiadiazole (acmtd) [**15**] and 2,6-diacetylaminopyridine (dacpy) [**16**] were prepared by literature methods.

2.2. Synthesis of the Na[bit]

NaOH (0.169 g, 4.233 mmol) in EtOH (10 cm^3) was added to benzoisothiazolinone (0.640 g, 4.233 mmol) suspended in EtOH (10 cm^3) and the resulting solution was stirred at room temperature for 30 min then filtered. The filtrate was reduced in volume by slow evaporation on a steam bath to afford a white solid which was collected and dried under vacuum (yield: 0.70 g, 95 %). mp: 300-302°C. IR (KBr): 3058w, 1685w, 1642m, 1566w,

1506vs, 1446m, 1348m, 1166m, 1014m, 729s, 671m, 617m cm^{-1}. ^1H NMR ($CDCl_3$): δ 81.9 (d, J 8.01, 1H), 7.66 (dd, J 7.60, 2H), 7.43-7.49 (m, 1H) ppm.

*2.3. Synthesis of $[Pd(bit)_2].H_2O$ (**1**)*

Na[bit] (0.117 g, 0.679 mmol) in MeOH (5 cm^3) was added to a solution of $Na_2[PdCl_4]$ (0.10 g, 0.33 mmol) in MeOH (8 cm^3). The brown mixture was stirred for 3 h and refluxed on a steam bath for 20 min. After cooling to room temperature, the red-brown solid formed was collected, washed with water and dried under vacuum (yield: 0.101 g, 70%). Anal. Calc. for $C_{14}H_{10}N_2O_3PdS_2$: C, 39.58; H, 2.37; 6.59. Found: C, 39.69; H, 2.49; N, 6.64. IR (KBr): 3551br, 3061w, 2917w, 1670w, 1633s, 1558vs, 1442m, 1311s, 491m, 442m, 410m cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.07 (d, J 8.0, 2H), 7.55 (d, J 8.1, 2H), 7.45-7.19 (m, 4H) ppm. Decomposes at 319 °C.

*2.4. Synthesis of $[Pt(bit)_2].H_2O$ (**2**)*

Na[bit] (0.041 g, 0.240 mmol) in EtOH (5 cm^3) was added to a solution of $K_2[PtCl_4]$ (0.050g, 0.120 mmol) in water (8 cm^3). The yellow mixture was stirred for 2 h and refluxed on a steam bath for 3 h. After cooling to room temperature, the pale yellow solid formed was collected, washed with water and dried under vacuum (yield: 0.051 g, 82 %). Anal. Calc. for $C_{14}H_{10}N_2O_3PtS_2$: C, 32.75; H, 1.96; 5.46. Found: C, 32.85; H, 2.08; N, 5.53. IR (KBr): 3425b, 3070w, 1663m, 1635vs, 1558vs, 1503m, 1441s, 1300s, 1244s, 1153m, 431m, 402s cm^{-1}. ^1H NMR (d^6-dmso): δ 7.86 (d, J 8.6, 2H), 7.75 (d, J 8.1, 2H), 7.68 (t, J 7.2, 2H), 7.48-7.21 (m, 2H) ppm. Decomposes at 312 °C.

*2.5. Synthesis of [Pd(bit)(tsac)] (**3**)*

Thiosaccharin (Htsac) (0.070 g, 0.353 mmol) in MeOH (5 cm^3) was added to a suspension of **1** (0.150 g, 0.353 mmol) in $CHCl_3$ (8 cm^3). The mixture was stirred for 3 h and refluxed on a steam bath for 10 min. The orange-red solid thus formed was collected, washed with EtOH and dried in a vacuum oven (yield: 0.128 g, 79 %). Anal. Calc. for $C_{14}H_8N_2O_3PdS_3$: C, 36.97; H, 1.77; N, 6.16. Found: C, 37.12; H, 1.96; N, 6.30%. IR (KBr); 3049w, 1632s, 1562m, 1443m, 1423m, 1016m, 804m, 439m, 413m cm^{-1}. ^1H NMR (d^6-

dmso): δ 7.95 (d, J 8.1, 1H, tsac), 7.89-7.73 (m, 5H, tsac & bit), 7.6 (t, J 7.5, 1H, bit), 7.41 (t, J 7.5, 1H, bit) ppm. Decomposes at 282 °C. .

*2.6. Synthesis of cis-[Pd(bit)$_2$(κ^2-bipy)] (**4**)*

2,2'-Bipyridine (bipy) (0.039 g, 0.254 mmol) in EtOH (5 cm^3) was added to a suspension of **1** (0.108 g, 0.254 mmol) in $CHCl_3$ (8 cm^3). The mixture was stirred for 3 h and refluxed on a steam bath for a further 3 h to give a yellow solution. This was filtered and the filtrate slowly evaporated to give an orange-yellow solid which was collected, washed with EtOH and dried in a vacuum oven (yield: 0.109 g, 76 %). Anal. Calc. for $C_{24}H_{16}N_4O_2PdS_2$: C, 51.20; H, 2.86; N, 9.95. Found: C, 51.28; H, 2.92; N, 9.99%. IR (KBr): 3058w, 1649vs, 1571vs, 1439m, 1305, 356w, 337m cm^{-1}. ^{1}H NMR (d^6-dmso): δ 8.55 (d, J 7.9, 2H, bit), 8.33 (d, J 7.9, 2H, bit), 7.95 (d, J 8.0, 2H, bipy), 7.85 (d, J 7.8, 2H, bipy), 7.81-7.69 (m, 4H, bit), 7.60 (t, J 7.5, 2H, bipy), 7.40 (t, J 7.5, 2H, bipy). Decomposes at 212 °C.

*2.7. Synthesis of trans-[Pd(bit)$_2$(dapy)$_2$] (**5**)*

2,6-Diaminopyridine (dapy) (0.031 g, 0.285 mmol) in EtOH (5 cm^3) was added to a suspension of **1** (0.0601 g ,0.142 mmol) in $CHCl_3$ (8 cm^3). The mixture was stirred at room temperature for 3 h. The pale yellow solid was collected, washed with EtOH and dried in a vacuum oven (yield: 0.066 g, 75 %). Anal. Calc. for $C_{24}H_{22}N_8O_2PdS_2$: C, 46.12; H, 3.55; N, 17.93. Found: C, 46.12; H, 3.67; N, 17.99%. IR (KBr): 3315m, 3147m, 3062w, 1647s, 1517vs, 1436m, 443w, 337w cm^{-1}. ^{1}H NMR (d^6-dmso): δ 7.64 (d, J 7.6, 4H, bit), 7.42 (t, J 7.7, 2H, bit), 7.27 (t, 7.6, 2H, bit), 6.97 (t, J 7.6, 2H, py), 5.59 (d, J 7.8, 4H, py), 5.26 (s, 8H, 4 NH_2). mp: 282-284°C**.**

*2.8. Synthesis of trans-[Pd(bit)$_2$(acmpy)$_2$] (**6**)*

2-Acetylamino-3-methylpyridine (acmpy) (0.043 g, 0.287 mmol) in EtOH (5 cm^3) was added to a suspension of **1** (0.061 g, 0.143 mmol) in chloroform (8 cm^3). The mixture was stirred at room temperature for 3 h to afford yellow solution. The solution was filtered and the filtrate slowly evaporated to give a pale-yellow solid which was collected, washed with EtOH and dried in a vacuum oven (yield: 0.084 g, 83 %). Anal. Calc. for

$C_{30}H_{28}N_6O_4PdS_2$: C, 50.96; H, 3.99; N, 11.88. Found: C, 51.03; H, 4.01; N, 11.91%. IR (KBr): 3277w, 3029w, 2920w, 1691s, 1646s, 1551vs, 1439m, 512m, 345m cm^{-1}. ^1H NMR (d^6-dmso): two isomers δ 13.17 (60%), 12.89 (40%) (s, 2H, NH), 9.92 (60%), 9.65 (40%) (s, 2H, py), 7.96-7.17 (m, 12H, bit, py), 2.13 (s, 6H, Me), 2.02 (s, 6H, Me) ppm. mp: 200-202°C**.**

*2.9. Synthesis of trans-[Pd(bit)$_2$(actz)$_2$] (**7**)*

2-Acetylaminothiazole (actz) (0.076 g, 0.539 mmol) in EtOH (5 cm^3) was added to a suspension of **1** (0.114 g, 0.269 mmol) in $CHCl_3$ (8 cm^3). The mixture was stirred at room temperature for 3 h. The resulting orange solution was filtered and the filtrate left to evaporate at room temperature to afford an orange–yellow solid. This was collected, washed with EtOH and dried in a vacuum oven (yield: 0.137 g, 74 %). Anal. Calc. for $C_{24}H_{20}N_6O_4PdS_4$: C, 41.71; H, 2.92; N, 12.16. Found: C, 41.81; H, 2.95; N, 12.19%. IR (KBr): 3348w, 3024w, 2920w. 1697s, 1649s, 1549vs, 1440m, 517m, 360s cm^{-1}: ^1H NMR (d^6-dmso): δ 12.2 (bs, 2H, 2NH), 8.50 (m, 10H, bit, actz), 7.16 (bs, 2H, actz), 2.20 (s, 6H, $2CH_3$) ppm. mp: 208-210°C**.**

*2.10. Synthesis of trans-[Pd(bit)$_2$(acbzt)$_2$] (**8**)*

2-Acetylaminobenzothiazole (acbzt) (0.076 g, 0.353 mmol) in EtOH (5 cm^3) was added to a suspension of **1** (0.075 g, 0.176 mmol) in $CHCl_3$ (8 cm^3). The mixture stirred at room temperature for 3h to give a yellow solution which was filtered. Slow evaporation gave an orange-yellow solid which was collected, washed with EtOH and dried in a vacuum oven (yield: 0.109 g, 78 %). Anal. Calc. for $C_{32}H_{24}N_6O_4PdS_4$: C, 48.57; H, 3.06; N, 10.62. Found: C, 48.60; H, 3.12; N, 10.69%. IR (KBr): 3275w, 3058w, 2918w, 1706s, 1647s, 1535vs, 1441s, 1307s, 511m, 349w cm^{-1}. ^1H NMR (d^6-dmso): δ 12.3 (bs, 2H, 2NH), 8.85-7.28 (m, 16H, bit, acbzt), 2.22 (s, 6H, $2CH_3$) ppm. mp: 240-242°C**.**

*4.11. Synthesis of trans-[Pd(bit)$_2$L$_2$] L = apy (**9**), acpym (**10**), abzt (**11**)*

Na[bit] (0.141 g, 0.814 mmol) in EtOH (8 cm^3) was added to a suspension of *trans*-[$PdCl_2$(apy)$_2$] (0.148 g, 0.407 mmol) in EtOH (8 cm^3). The mixture was stirred for 3 h to afford a yellow precipitate, which was collected, washed with water and EtOH and dried

under vacuum (yield: 0.225 g, 93 %). Anal. Calc. for $C_{24}H_{20}N_6O_2PdS_2$: C, 45.56; H, 2.82; N, 11.19. Found: C, 45.69; H, 2.99; N, 11.33 %. IR (KBr): 3409s, 3327m, 3096w, 1649vs, 1573s, 1494m, 1442m, 1326m, 408m, 376m, 330m cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.08 (s, 4H, py), 8.07 (s, 4H, py), 7.83-7.68 (m, 8H, bit), 7.48 (s, 4H, $2NH_2$) ppm. Decomposes at 287 °C.

The following complexes were prepared and isolated by a similar method:

*trans-[Pd(bit)$_2$(acpym)$_2$] **(10)**.* Pale red solid. Yield 0.098 g (66 %)**.** Anal. Calc. for $C_{26}H_{22}N_8O_4PdS_2$: C, 45.85; H, 3.26; N, 16.45. Found: C, 45.97; H, 3.37; N, 16.60 %. IR (KBr): 3431w, 3076w, 2920w, 1697m, 1649vs, 1580s, 1508m, 1438m, 489m, 418s, 345w cm^{-1}. ^1H NMR (d^6-dmso): δ 10.56 (s, 2H, 2NH), 8.63 (d, J 4.7, 4H, pym), 7.65-6.53 (m, 8H, bit), 7.14 (t, J 4.7, 2H, pym), 2.13 (s, 6H, Me) ppm. mp: 318-320°C.

*trans-[Pd(bit)$_2$(abzt)$_2$] **(11)**.* Light yellow solid. Yield 0.166 g (76 %). Anal. Calc. for $C_{28}H_{20}N_6O_2PdS_4$: C, 47.56; H, 2.98; N, 12.4. Found C, 47.70; H, 2.98; N, 12.04 %. IR (KBr): 3434s, 3346s, 3063w, 2929w, 1647s, 1544vs, 1454m, 1437m, 1303m, 437m, 332m cm^{-1}. ^1H NMR (d^6-dmso): δ 7.70 (d, J 7.8, 2H, abzt), 7.59 (d, J 7.5, 2H, bit), 7.54 (d, J 7.8, 2H, bit), 7.46 (bs, 4H, $2NH_2$), 7.33 (d, J 7.7, 2H, abzt), 7.29 (t, J 7.4, 2H, abzt), 7.18 (t, J 8.1, 2H, abzt), 7.12 (t, J 8.2, 2H, bit), 6.97 (t, J 8.2, 2H, abzt) ppm. Decomposes at 277 °C.

*2.12. Synthesis of trans-[Pd(bit)$_2$(dacpy)] **(12)***

2,6-Diacetoamidepyridine (dacpy) (0.059 g, 0.308 mmol) in EtOH (5cm^3) was added to a suspension of **1** (0.131 g, 0.308 mmol) in $CHCl_3$ (8 cm^3). The mixture was stirred for 3 h to afford a brown precipitate, which was filtered, washed with EtOH and dried in a vacuum oven (yield: 0.123 g, 70 %). Anal. Calc. for $C_{23}H_{19}N_5O_4PdS_2$: C, 48.47; H, 3.36; N, 9.83. Found: C, 48.58; H, 3.41; N, 9.89%. IR (KBr): 3323w, 3240w, 1664s, 1643vs, 1560s, 1441m, 1303m, 330w cm^{-1}. ^1H NMR (d^6-dmso): δ 10.05 (s, 2H, 2NH), 7.71 (d, J 7.8, 2H, py), 7.65 (t, J 8.1, 1H, py), 7.65-7.12 (m, 8H, bit), 2.07 (6H, Me) ppm. mp: 278-280 °C**.**

*2.13. Synthesis of [Pd(bit)$_2$(acmtd)] **(13)***

A suspension of 2-acetylamino-5-methyl-1,3.4-thiadiazol (acmtd) (0.027 g, 0.172 mmol) in EtOH (8cm^3) was added to a suspension of **1** (0.073g , 0.172 mmol) in $CHCl_3$ (8cm^3). The mixture was stirred for 3 h and refluxed on a steam bath for a further 20 min to give a yellow solution. This was filtered and the filtrate set aside to slowly evaporate to afford a pale-yellow solid which was collected by filtration, washed with EtOH and dried (yield: 0.069 g, 72%). Anal. Calc for $C_{19}H_{15}N_5O_3PdS_3$: C, 40.46; H, 2.68; N, 12.42. Found: C, 40.49; H, 2.72; N, 12.49%. IR (KBr): 3244w, 3055w, 1685s, 1652vs, 1552vs, 1440s, 13011s, 426m, 341m cm^{-1}. ^{1}H NMR (d^6-dmso): δ 12.35 (s, 1H, NH), 7.57 (brs, 4H, bit), 7.29 (brs, 2H, bit), 7.13 (brs, 2H, bit), 2.79 (s, 3H, MeCO), 2.15 (s, 3H, Me). Decomposes at 302°C.

*2.14. Synthesis of trans-[Pd(bit)$_2$(PPh$_3$)$_2$] (**14**)*

PPh_3 (0.068 g, 0.260 mmol) in $CHCl_3$ (5 cm^3) was added to **1** (0.055 g, 0.130 mmol) suspended in $CHCl_3$ (8 cm^3). The brown red mixture was stirred for 2 h at room temperature and refluxed on a steam bath for 20 min to afford a yellow-orange precipitate, which was collected and dried under vacuum (yield: 0.085 g, 71 %). Anal. Calc. for $C_{50}H_{38}N_2O_2PdP_2S_2$: C, 64.48; H, 4.11; N, 3.01. Found: C, 64.64; H, 4.25; N, 3.15%. IR (KBr): 3053m, 1652vs, 1571s, 1434s, 1303m, 1114m, 1188m, 511s, 400m, 369m cm^{-1}. ^{31}P{^{1}H} NMR ($CDCl_3$): δ 29.0 ppm. ^{1}H NMR ($CDCl_3$): δ 7.80 (bm, 10H, Ph), 7.78 (q, J 7.8, 2H, Ph), 7.28 (d, J 7.8, 2H, bit), 7.2 (m, 4H, Ph), 7.17 (bs, 14H, Ph), 7.03 (t, J 7.8, 2H, bit), 6.97 (d, J 7.8, 2H, bit), 6.87 (t, J 7.8, 2H, bit) ppm. Decomposes at 202 °C.

*2.15. Synthesis of cis-[Pd(bit)$_2$(κ^2-dppe)] (**15**)*

Na[bit] (0.0315 g, 0.182 mmol) in EtOH (5 cm^3) was added to [$PdCl_2$(κ^2-dppe)] (0.0526 g, 0.086 mmol) suspended in CH_2Cl_2 (10 cm^3). The mixture was stirred 2 h and heated on a steam bath for 20 min. The yellow solution thus formed was filtered and the filtrate left to evaporate at room temperature to afford yellow needle-like crystals which were collected and dried under vacuum (yield: 0.062 g, 85 %). Alternatively, a solution of dppe (0.056 g, 0.141 mmol) in $CHCl_3$ (5 cm^3) was added to a suspension of **1** (0.060 g, 0.141 mmol) in $CHCl_3$ (10 cm^3). The red mixture was stirred and heated on a steam bath for 30 min. The resulting orange solution was filtered and the filtrate was slowly evaporated to afford orange-yellow needle-like crystals which were collected and dried under vacuum

(yield: 0.091 g, 80 %). Anal. Calc. for $C_{40}H_{32}N_2O_2PdP_2S_2$: C, 59.67; H, 4.01; N, 3.48. Found: C, 59.40; H, 4.17; N, 3.50%. IR (KBr): 3389br, 3055w, 2910w, 1652s, 1436s, 1307m, 1103m, 530m, 499m, 313w, 350m cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 57.8. ^1H NMR ($CDCl_3$): δ 7.95-7.87 (m. 8H, Ph), 7.64 (d, J 8.0, 2H, bit), 7.46-7.20 (m, 16H, Ph, bit), 7.06 (t, J 8.0, 2H, bit), 2.48 (d, J 10.0, 2H, CH_2), 2.43 (d, J 10.0, 2H, CH_2) ppm.

*2.16. Synthesis of cis-[Pd(bit)$_2$(κ^2-dppp)] (**16**)*

Na[bit] (0.011 g, 0.180 mmol) in EtOH (5 cm^3) was added to [$PdCl_2$(κ^2-dppp)] (0.053 g, 0.090 mmol) suspended in CH_2Cl_2 (10 cm^3). The mixture was stirred for 2 h at room temperature and heated on a steam bath for 3 h. The yellow solution thus formed was filtered and the filtrate evaporates slowly to give yellow needle-like crystals which were collected and dried under vacuum (yield: 0.054 g, 74 %). Alternatively, dppp (0.058 g, 0.141 mmol) in $CHCl_3$ (5 cm^3) was added to **1** (0.060 g, 0.141 mmol) suspended in $CHCl_3$ (10 cm^3). The red mixture was stirred a room temperature for 3 h and heated on a steam bath for 3 h until it became clear. The yellow solution was filtered and the filtrate evaporated slowly to give yellow needle-like crystals which were collected and dried under vacuum (yield: 0.083 g, 72 %). Anal. Calc. for $C_{41}H_{34}N_2O_2PdP_2S_2$: C, 60.11; H, 4.18; N, 3.42. Found: C, 60.33; H, 3.36; N, 3.60%. IR (KBr): 3359m, 3274w, 1650s, 1556vs 1438s, 1307m, 1101m, 692m, 510m, 356m, 314m cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 5.6 ppm. ^1H NMR ($CDCl_3$): δ 7.77-7.09 (28H, bit, Ph), 2.61 (bs, 4H, $2CH_2$), 2.14 (bs, 2H, CH_2) ppm. mp: 215-217 ^oC.

2.17. Reaction of [$PdCl_2$(κ^2-dppb)] with 2 Na[bit]

Na[bit] (0.029 g, 0.170 mmol) in EtOH (5 cm^3) was added to [$PdCl_2$(κ^2-dppb)] (0.051 g, 0.085 mmol) suspended in CH_2Cl_2 (10 cm^3). The mixture formed was stirred for 2 h and heated on a steam bath for 1 h .The yellow solution thus formed was filtered and the filtrate evaporated slowly to give orange-yellow solid which was collected and dried under vacuum (yield: 0.062 g, 78 %). IR (KBr): 3051m, 2920m, 1650vs, 1560s, 1433s, 1306m, 1101m, 904m, 696s, 499m, 331m, 311w cm^{-1}. The $^{31}P\{^1H\}$ NMR spectrum of the product indicated that it is a mixture of two compounds; monosubsituted [Pd(bit)Cl(κ^2-dppb)] (**18**) (*ca.* 40 %) [$^{31}P\{^1H\}$NMR: δ 42.7 (d, J 19, P_A), 8.0 (d, J 19, P_B)] and disubstituted [Pd(bit)$_2$(κ^2-dppb)] (**17**) (*ca.* 60 %) [$^{31}P\{^1H\}$ NMR: δ 22.5 (s)]. ^1H NMR ($CDCl_3$) (mixture) δ 7.92-7.02 (m, 28H,

bit, Ph), 2.76 (bs, 2H, CH_2), 2.54 (bs, 2H, CH_2), 2.10 (bs, 2H, CH_2) ppm. Decomposes at 152 °C.

2.18. Reaction of $[Pd(bit)_2].H_2O$ with dppm

Dppm (0.074 g, 0.192 mmol) in $CHCl_3$ (5cm^3) was added to **1** (0.082 g, 0.192 mmol) suspended in $CHCl_3$ (8 cm^3). The mixture was stirred for 3 h and heated on a steam bath for 30 min until it became yellow. The solution was filtered and the filtrate evaporated at room temperature to afford a yellow-orange solid, which was collected and dried under vacuum (yield: 0.115 g). The $^{31}P\{^1H\}$ NMR spectrum in $CDCl_3$ indicated that the product is a mixture of three complexes; $[Pd(bit)_2(\kappa^2\text{-dppm})]$ (**19**) (55%) [$^{31}P\{^1H\}$NMR: δ 46.5(s)], $[Pd_2(bit)_4(\mu\text{-dppm})_2]$ (**21**) (40%) [$^{31}P\{^1H\}$NMR: δ 24.7(s)] and *trans*-$[Pd(bit)_2(\kappa^1\text{-dppm})_2]$ (**20**) (5%) [$^{31}P\{^1H\}$NMR: δ 46.4 (d, J 48), 15.7 (d, J 48)].

2.19. Reaction of $[PdCl_2(\kappa^2\text{-dppm})]$ with 2 Na[bit]

Na[bit] (0.0343 g, 0.198 mmol) in EtOH (5 cm^3) was added to $[PdCl_2(\kappa^2\text{-dppm})]$ (0.0557 g, 0.099 mmol) suspended in CH_2Cl_2 (10 cm^3). The mixture was stirred at room temperature for 3 h and refluxed on a steam bath for 1 h. The yellow solution was filtered and the filtrate evaporated slowly at room temperature. The yellow solid thus formed was collected and dried under vacuum (yield: 0.058 g). Anal. Calc. for $C_{39}H_{30}N_2O_2PdP_2S_2$: C, 59.21; H, 3.82; N, 3.54. Found: C, 59.41; H, 4.17; N, 3.50%. IR (KBr): 3051w, 2920m, 1652s, 1558vs, 1436s, 1307m, 1101s, 694m, 503m, 413m, 355m, 310m cm^{-1}. The $^{31}P\{^1H\}$ NMR spectrum in $CDCl_3$ showed a mixture of $[Pd(bit)_2(\kappa^2\text{-dppm})]$ (**19**) (90 %) and $[Pd_2(bit)_4(\mu\text{-dppm})_2]$ (**21**) (10 %). ^1H NMR ($CDCl_3$): δ 7.88-7.83 (m, 8H, bit), 7.47-7.20 (m, 20H, Ph), 4.11 (t, J 9.4, 2H, CH_2).

2.20. Reaction of $[Pd(\kappa^2\text{-dppm})_2]Cl_2$ with 2Na[bit]

Na[bit] (0.0219 g, 0.126 mmol) in EtOH (8 cm^3) was added to a solution of $[Pd(dppm)_2]Cl_2$ (0.060 g, 0.0634 mmol) in EtOH (8 cm^3). The orange suspension was stirred at room temperature for 3 h and heated on a steam bath for 1 h until it became clear. The

solution was filtered and the filtrate left to evaporate at room temperature to afford a yellow-orange solid. The solid was collected and dried under vacuum (yield: 0.052 g). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$) spectrum of the product showed to be a mixture of **20** (80 %) and **21** (20 %).

*2.21. Molecular structure determination of **15**.2EtOH*

Yellow crystals of [Pd(bit)$_2$(κ^2-dppe)].2EtOH suitable for X-ray crystallography were produced by slow evaporation of a saturated CH_2Cl_2-EtOH solution. A yellow crystal with approximate dimensions 0.50 x 0.11 x 0.06 mm^3 was mounted on a glass fiber and all geometric and intensity data were taken from this sample using a STOE-IPDS diffractometer with Mo-Kα radiation (λ = 0.7103 Å, graphite monochromator). Absorption corrections were made using the IPDS software package [**17**]. All structures were solved by direct methods and refined using full-matrix least-square routines against F^2 with SHELXL-97 [**18**]. 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. The two solvent molecules are disordered. Illustrations were generated using DIAMOND 3.0 [**19**].

3. Results and discussion

3.1. Synthesis of [M(bit)$_2$].H$_2$O (M = Pd, Pt) and [Pd(bit)(tsac)]

Reaction of two equivalents of Na[bit] with $Na_2[PdCl_4]$ in methanol afforded [Pd(bit)$_2$].H$_2$O (**1**) as a red-brown solid in 70 % yield after simple workup, and a similar reaction of Na[bit] with $K_2[PtCl_4]$ gave [Pt(bit)$_2$].H$_2$O (**2**) as a pale yellow solid in 82 % yield. ^{1}H NMR spectra were recorded in $CDCl_3$ (**1**) and d^6-dmso (**2**) and are consistent with the addition of benzisothiazolinate to the metal centre but otherwise uninformative, and formulations were based predominantly on analytical data which are consistent with the inclusion of one water molecule per metal atom. We have been unable to obtain X-ray crystallographic quality samples and thus precise structures remain unknown. Similar behavior *viz*. their relatively poor solubility in common organic solvents and inclusion of one water per metal atom, is seen in related tsac complexes [M(tsac)$_2$].H$_2$O (M = Pd, Pt) [**20**]. On the basis of the data that we have we cannot discern between monomeric (**A**) and dimeric (**B**)

structural motifs (Chart 2) or indeed a polymeric structure (not shown) but we discount the latter on the basis of their solubility in organic solvents. We favour a dimeric structure **B** as this will greatly reduce ring-strain and it is likely that water molecules are bound to both metal centers.

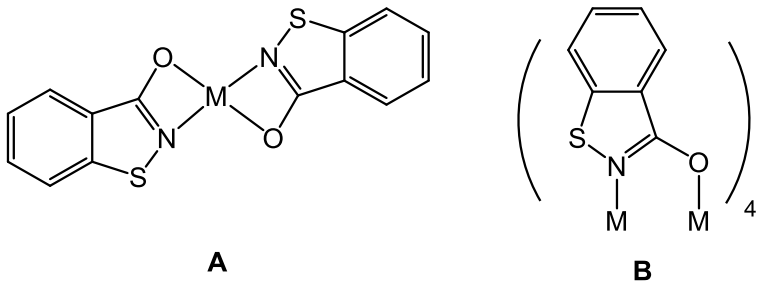
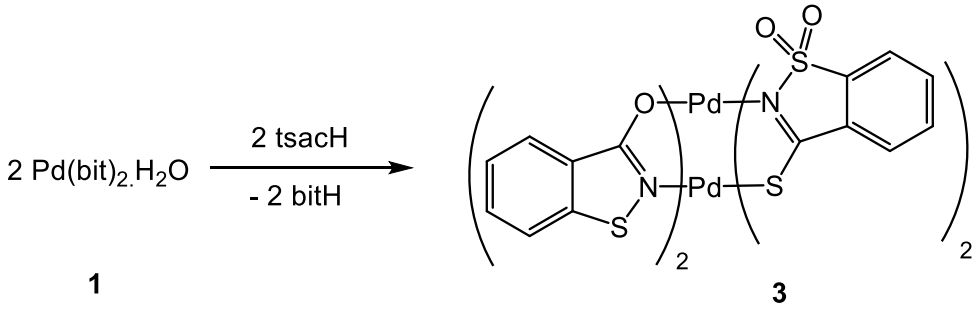


Chart 2

Reaction of $[Pd(bit)_2].H_2O$ (**1**) with one equivalent of thiosaccharin (tsacH) gave a new orange-red solid characterised as [Pd(bit)(tsac)] (**3**) in 79 % yield. The ^1H NMR spectrum confirms the exchange of one benzisothiazolinate group for a thiosaccharinate ligand. It also shows that there is a single environment for both bit and tsac ligands and this is most consistent with either a monomeric complex, or a symmetrical binuclear complex (shown). Elemental analysis is most consistent without added water, however, it could simply be that this removed during the drying process.

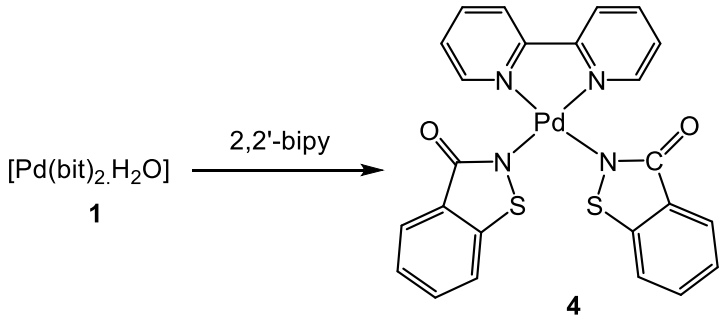


Scheme 1

3.2. Reactions of $[Pd(bit)_2].H_2O$ with amines

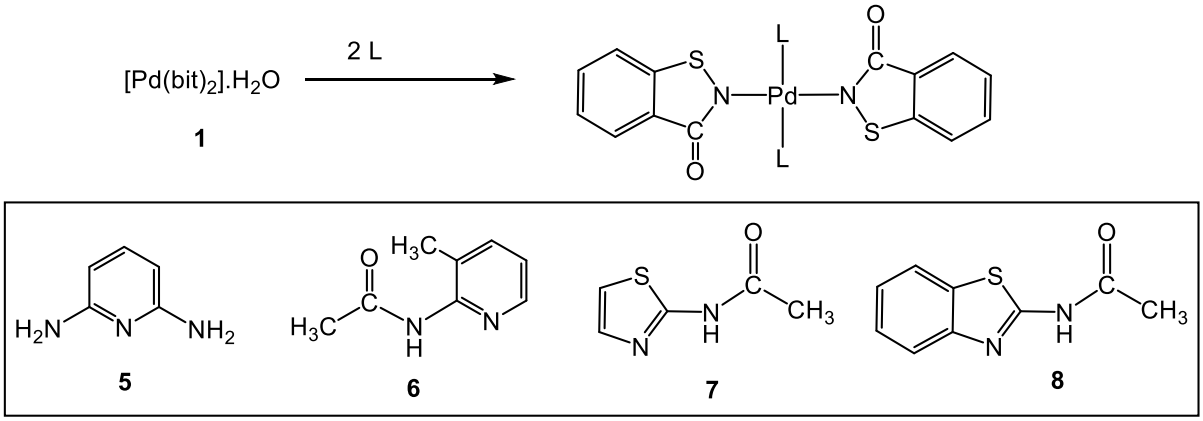
As discussed in the introduction, Griffith and co-workers have prepared the amine complexes *cis*-$[Pd(bit)_2(\kappa^2\text{-en})]$ (en = ethylenediamine) and *cis*-$[Pt(NH_3)_2(bit)_2]$ [**11**]. In order to develop complexes of this type we initially reacted $[Pd(bit)_2].H_2O$ (**1**) with 2,2'-bipyridine (bipy) and this gave *cis*-$[Pd(bit)_2(\kappa^2\text{-bipy})]$ (**4**) as a yellow solid in 76 % yield (Scheme 2).

The ^{1}H NMR spectrum in d^6-dmso clearly shows that the ratio of benzisothiazolinate and diamine ligands is 2:1 and is in accord with that found for *cis*-[Pd(bit)$_2$(κ^2-en)] [**11**]. Thus we conclude that the 2,2-bipyridine ligand binds in a chelate manner thus forcing the benzisothiazolinate ligands *cis*.



Scheme 2

[Pd(bit)$_2$].H$_2$O (**1**) reacts directly with 2,6-diaminopyridine (dapy) at room temperature to yield a yellow precipitate formulated as *trans*-[Pd(bit)$_2$(dapy)$_2$] (**5**) in 75 % yield (Scheme 3). Elemental analysis is consistent with addition of two equivalents of dapy and assignment as the *trans* isomer is based mainly on the IR spectrum, which is relatively simple in accord with the higher symmetry and also in accord with the other complexes of the type *trans*-[Pd(bit)$_2$L$_2$] (see below). The ^{1}H NMR spectrum was recorded in d^6-dmso and is fully consistent with the proposed structure. It is noteworthy that in both of these amino-pyridine complexes a single isomer is observed in solution as shown by the observation of a singlet a δ 5.26 associated with the eight amino-protons.



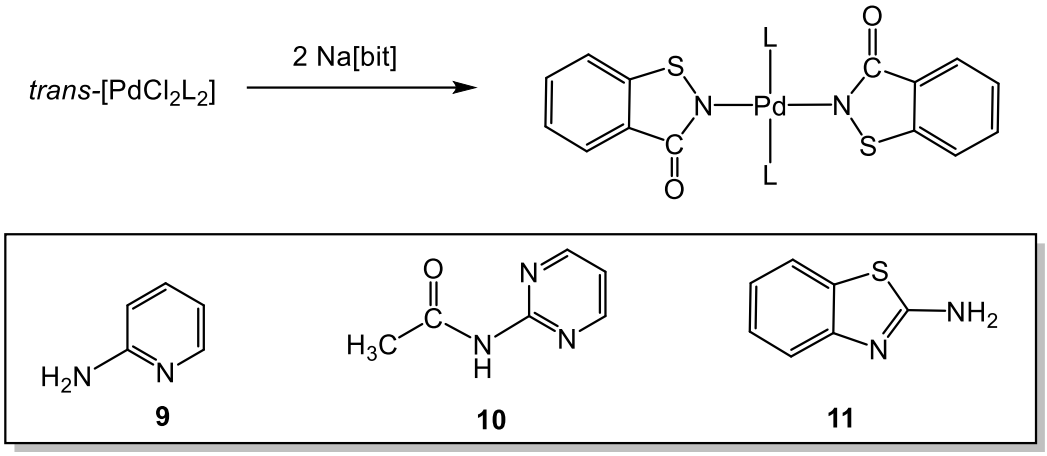
Scheme 3

Reaction of 2-acetylamino-3-methylpyridine (acmpy) with **1** gave a pale yellow solid in 83 % yield formulated as *trans*-[Pd(bit)$_2$(acmpy)$_2$] (**6**). The ^{1}H NMR spectrum suggests the co-existence of two non-interconverting isomers in solution. Thus (in d^6-dmso) duplicate signals for the NH and H_6 (of the pyridine ring) protons are observed in a *ca.* 3:2 ratio. Such isomerism in solution has previously been noted for the related saccharinate complexes *trans*-[Pd(sac)$_2$(2-aampy)$_2$] and *trans*-[Pd(sac)$_2$(abzt)$_2$] (2-aampy = 2-acetylaminopyridine; abzt = 2-aminobenzothiazole) [**21,22**] and is attributed to the presence of isomers differing in the relative orientation of saccharinate and pyridine ligands.

Both 2-acetylaminothiazole (actz) and 2-acetylaminobenzothiazole (acbzt) add cleanly to **1** to afford *trans*-[Pd(bit)$_2$(actz)$_2$] (**7**) and *trans*-[Pd(bit)$_2$(acbzt)$_2$] (**8**) in 74 and 78 % yields respectively. The ^{1}H NMR spectrum of **7** is not very informative**.** The two amine protons appear as a broad singlet at δ 12.2 and the two methyl groups of the actz ligand are equivalent as shown by a singlet resonance at δ 2.20. Similarly the ^{1}H NMR spectrum of **8** contains a broad singlet at δ 12.3 and a singlet at δ 2.22. These observations are in accord with either the facile rotation about Pd-N bonds or the selective isolation of a single isomer and unfortunately we are not in a position to determine this.

3.3. Reactions of trans-[PdCl$_2$L$_2$] with sodium benzisothiazolinate

An alternative route to benzisothiazolinate complexes is the pre-coordination of the supporting ligand and introduction of one or more benzisothiazolinate ligands *via* nucleophilic substitution. Thus *trans*-[PdCl$_2$(apy)$_2$] [**20**] was reacted with two equivalents of Na[bit] in EtOH to give a yellow precipitate characterised as *trans*-[Pt(apy)$_2$(bit)$_2$] (**9**) (Scheme 4). The complex is soluble in $CDCl_3$ and a ^{1}H NMR spectrum confirmed the 1:1 ratio of amine and benzisothiozolinate ligands. That coordination of 2-aminopyridine is monodentate is confirmed by the observation of a singlet at 7.48 ppm in the ^{1}H NMR spectrum assigned to the two uncoordinated amine groups. Similarly Na[bit] reacts with *trans*-[PdCl$_2$(acpym)$_2$] [**23**] (acpym = acetylaminopyrimidine) to afford a pale red solid formulated as *trans*-[Pd(bit)$_2$(acpym)$_2$] (**10**) and with *trans*-[PdCl$_2$(abzt)$_2$] [**23**] (abzt = 2-aminobenzothiazole) to yield yellow *trans*-[Pd(bit)$_2$(abzt)$_2$] (**11**). Spectral data are unexceptional and consistent with the proposed elemental formulations.



Scheme 4

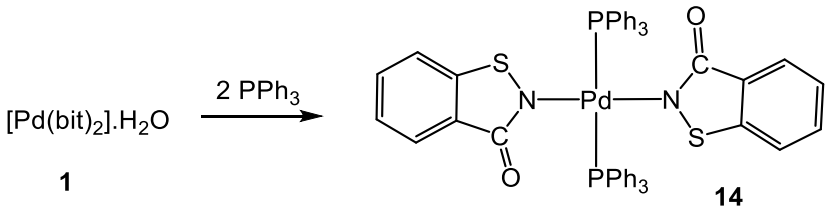
3.4. Reactions of 1 with 2,6-diacetoaminopyridine (dacpy) and 2-acetylamino-5-methyl-1,3.4-thiadiazol (acmtd)

Acetylated 2,6-diacetoaminopyridine (dacpy) reacts with **1** to afford a complex of stoichiometry $[Pd(bit)_2(dacpy)]$ (**12**) in 70 % yield, while a complex with a similar 2:1 ratio of benzisothiazolinate and added ligand namely $[Pd(bit)_2(acmtd)]$ (**13**) resulted from reaction of **1** with 2-acetylamino-5-methyl-1,3.4-thiadiazol (acmtd). The precise structures of these two species remain unknown and all attempts to grow crystals suitable for X-ray diffraction have been unsuccessful. Their stoichiometry is primarily derived from elemental analyses but confirmed by the relative ratios of the two ligand types in the ^{1}H NMR spectra. For **12** the latter is very simple and suggests either a symmetrical complex or one which is highly fluxional on the NMR timescale at room temperature. Thus, while it is tempting to suggest that the 2,6-diacetoaminopyridine (dacpy) ligand binds in a bidentate fashion, it is difficult to see how this would not give rise to a complex spectrum for the dacpy ligand, when signals for the latter are simple and consistent with a plane of symmetry. This could be achieved for a binuclear complex in which two dacpy ligands span the metal-metal vector. We have recently reported the synthesis and crystal structure of the metallamacrocyclic complex, $[Hg_2(\mu\text{-}2,6\text{-}dacpy(\text{-}H)_2)_2]$ [**24**], in which the two Hg(II) centers are spanned by a pair of doubly deprotonated 2,6-diacetoaminopyridine ligands. In **12** the observation of a singlet at δ 10.05 suggests that here such a deprotonation has not occurred but nevertheless this does provide some evidence for a structure of the type $[Pd(bit)_2(\mu\text{-}dacpy)]_2$ and in the absence of a molecular structure we feel that this best fits the observed data. NMR data for **13** are also consistent with a symmetrical structure. Thus three signals are seen for the

benzisothiazolinate protons in a ratio of 2:1:1. All are broadened and this may be associated with some degree of fluxionality.

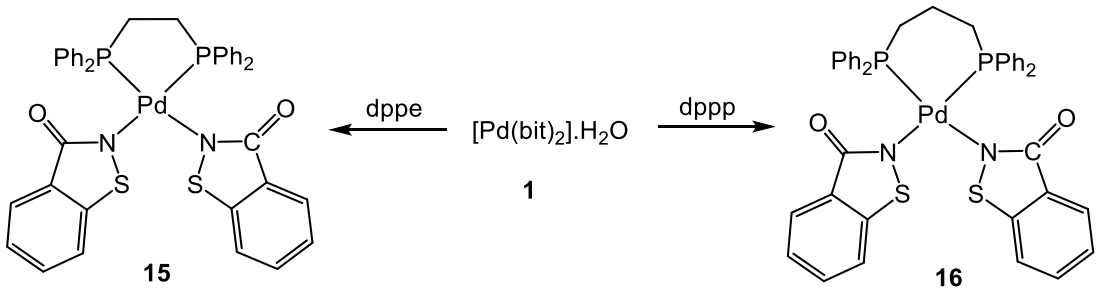
3.5. Reactions of [Pd(bit)$_2$].H$_2$O with PPh$_3$ and Ph$_2$P(CH$_2$)$_n$PPh$_2$ (n = 2, 3)

Heating a mixture of **1** and two equivalents of PPh_3 in chloroform afforded a yellow-orange precipitate characterised as *trans*-[Pd(bit)$_2$(PPh$_3$)$_2$] (**14**) in 71% yield (Scheme 5). The $^{31}P\{^1H\}$ NMR spectrum consists of only of a singlet at 29.0 ppm. While both *cis* and *trans* arrangements of the two phosphine ligands are consistent with the observed NMR data we favour the latter, primarily on the basis of the relatively simple nature of the IR spectrum which would suggest a high symmetry system. This arrangement also minimizes adverse steric interactions between the bulky PPh_3 ligands and would be favoured on steric grounds.



Scheme 5

A similar reaction between equimolar amounts of **1** and 1,2-bis(diphenylphosphino)ethane (dppe) yielded *cis*-[Pd(bit)$_2$(κ^2-dppe)] (**15**) in 80% yield (Scheme 6). Alternatively, **15** could be prepared in comparable yields upon addition of two equivalents of Na[bit] to [PdCl$_2$(κ^2-dppe)] at room temperature. Here the *cis* arrangement of the two benzisothiazolinate ligands is imposed by the chelating diphosphine.



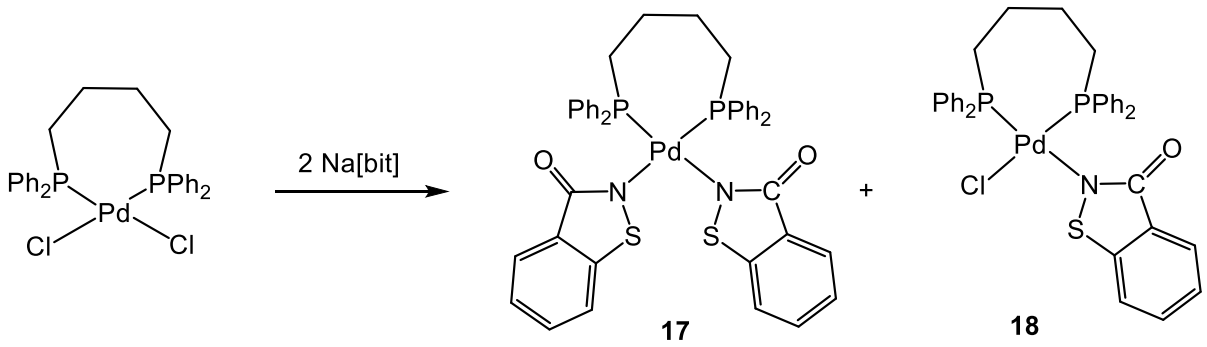
Scheme 6

Crystallization of **15** upon slow evaporation of a saturated CH_2Cl_2/EtOH solution gave yellow needles suitable for X-ray crystallography. The molecular structure is shown in Figure 1. The palladium center adopts a slightly distorted square planar geometry with N(1)-Pd-N(2) and P(1)-Pd-P(2) bonds angle of 92.36(11)^o and 84.41(4)^o respectively, The two benzisothiazolinate anions are each coordinated in a monodentate fashion through nitrogen, being orientated approximately perpendicular to the PdN_2P_2 plane and in a relative "up-down" arrangement such that the carbonyls lie on opposite sides of the PdN_2P_2 plane. The Pd-N(1) and Pd-N(2) bonds lengths of 2.070(3) and 2.100(3) Å respectively lie within the normal range of the Pd-N interactions, and compare well with those in *cis*-[Pd(bit)$_2$(κ^2-en)] [**11**]. Likewise, the Pd-P bond lengths of 2.234(1) and 2.230(1) Å lie within the normal range of the Pd(II)-P interactions**.**

In a similar way to the synthesis of **15**, reaction of **1** and 1,3-bis(diphenylphosphino)propane (dppp) or addition of Na[bit] to [PdCl$_2$(κ^2-dppp)] afforded *cis*-[Pd(bit)$_2$(κ^2-dppp)] (**16**) in 72-74 % yields. Characterizing data for **16** are fully in accord with those of **15**. The $^{31}P\{^1H\}$ NMR spectrum of the latter showed a singlet resonance at 57.8 ppm, while for the dppp complex **16** a singlet appeared at 5.6 ppm. The ^1H NMR spectra of both were relatively uninformative, consisting of complex multiplets in the aromatic regions and signals between δ 2.6-2.1 associated with the methylene backbones of the diphosphine ligands. Unfortunately due to the overlapping nature of the aromatic responses we were unable to say for certain whether the two benzisothiazolinate are inequivalent in solution (as seen in the solid state).

3.6. Preparation of cis-[Pd(bit)$_2$(κ^2-dppb)] and cis-[PdCl(bit)(κ^2-dppb)]

In an attempt to extend this chemistry to 1,4-bis(diphenylphosphino)butane (dppb) we reacted [PdCl$_2$(κ^2-dppb)] with two equivalents of Na[bit]. After work-up a mixture of two inseparable products was resulted as shown by $^{31}P\{^1H\}$ NMR spectroscopy (Scheme 7). The major species (*ca.* 60%) was characterised by a singlet at 22.5 ppm and we attribute this to the target product, namely *cis*-[Pd(bit)$_2$(κ^2-dppb)] (**17**). The second species is characterised by a pair of doublets (J_{PP} 19 Hz) at 42.7 and 8.03 ppm which we associate with the part-substituted complex *cis*-[Pd(bit)Cl(κ^2-dppb)] (**18**), the difference in chemical shift between the two ends of the diphosphine being attribute to the *trans* influence of chloride and amide ligands.



Scheme 7

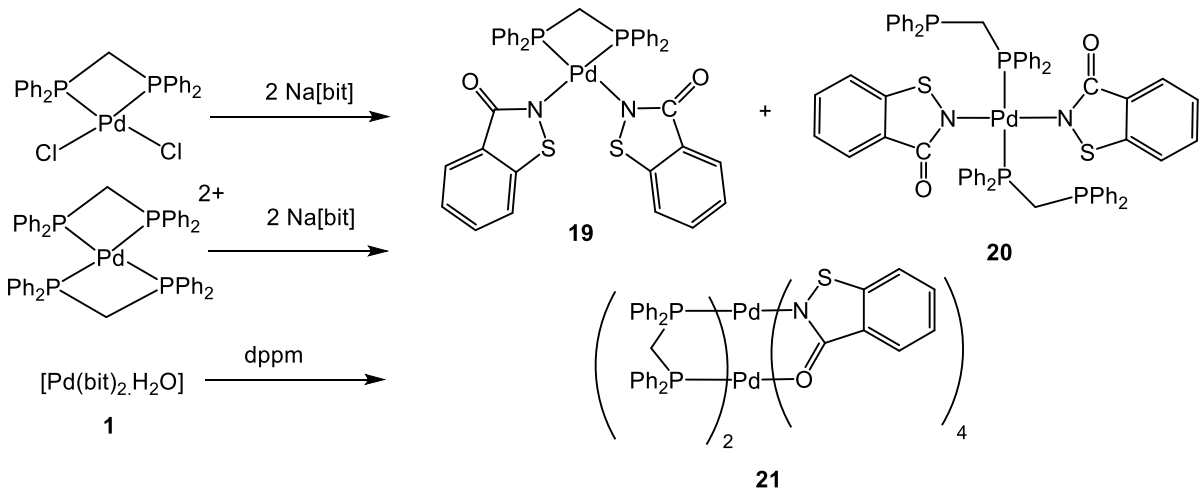
3.7. Preparation of cis-[Pd(bit)$_2$(κ^2-dppm)] and other dppm-bit complexes

Attempts to prepare derivatives of the small-bite angle diphosphine ligand bis(diphenylphosphino)methane (dppm) analogous to **15-17** were more complicated. Reaction of **1** with dppm in chloroform afforded a yellow-orange solid which was shown to be a mixture of at least three new complexes by $^{31}P\{^1H\}$ NMR spectroscopy. The major species in solution (*ca.* 55%) exhibited a singlet resonance at -46.5 ppm and we tentatively assign this to the target product *cis*-[Pd(bit)$_2$(κ^2-dppm)] (**19**) as it is well-documented that constraining dppm into a four-membered ring results in a significant up-field shift of the ^{31}P chemical shift [**25,26**]. The next major species (*ca.* 40%) is characterised by a singlet at 24.7 ppm. This region of the spectrum is typically associated with the ligand acting in a bridging capacity [**25,26**] and we thus (very) tentatively assign this to the dipalladium species [Pd$_2$(bit)$_4$(μ-dppm)$_2$] (**21**). A third minor species is characterised by a pair of doubles (J_{PP} 48 Hz) at 46.4 and 15.7 ppm. The nature of this material is less well understood but we very tentatively suggest a mononuclear species [Pd(bit)$_2$(κ^1-dppm)$_2$] (**20**) in which one end of the diphosphine is metal coordinated and the other end is free. We are unable to say whether this contains a *cis* or *trans* arrangement of the benzisothiazolinate but we favour the latter.

In seeking to gain further insight into the nature of all three products from the above reaction, we also looked at the reaction of [PdCl$_2$(κ^2-dppm)] with two equivalents of Na[bit] anticipating that this would provide a clean route to **19**. Indeed the major species (*ca.* 90%) was **19** and we were also able to record a ^1H NMR spectrum which showed the expected triplet for the methylene backbone at δ 4.11 (J_{PH} 9.36 Hz). The reaction was not however totally clear and we have been unable to separate the minor constituents to arrive at a pure sample of **19**. An elemental analysis of the mixture did, however, fit the proposed

formulation of **19** suggesting that the minor component had a bit to diphosphine ratio of *ca.* 2:1. This second component (*ca.* 10%) was characterized by a singlet at 24.8 ppm in the $^{31}P\{^{1}H\}$ NMR spectrum being associated with binuclear **21**. We have also studied the reaction of $[Pd(\kappa^2\text{-dppm})_2]Cl_2$ with two equivalents of Na[bit] as this potentially leads to the formation of $[Pd(bit)_2(\kappa^1\text{-dppm})_2]$ (**20**). Stirring at room temperature in ethanol afforded a yellow-orange solid the major component of which (*ca.* 80%) was **18** on the basis of the $^{31}P\{^{1}H\}$ NMR spectrum. The second species (*ca.* 20%) is **21** appearing only as a singlet at 24.7 ppm.

Thus in summary the above experiments lead us to conclude with some confidence that *cis*-$[Pd(bit)_2(\kappa^2\text{-dppm})]$ (**19**) and $[Pd(bit)_2(\kappa^1\text{-dppm})_2]$ (**20**) are the major products from reactions of $[PdCl_2(\kappa^2\text{-dppm})]$ and $[Pd(\kappa^2\text{-dppm})_2]Cl_2$ respectively with two equivalents of Na[bit]. Reaction of **1** with dppm appears to be less selective and leads together with **19** and **20** to the generation of a third species somewhat more tentatively assigned as $[Pd_2(bit)_4(\mu\text{-dppm})_2]$ (**21**) which is also formed in small amounts in the other two reactions.



Scheme 8

4. Summary and conclusions

We have illustrated in this work that palladium(II) benzisothiazolinate complexes of the type $[Pd(bit)_2L_2]$ are easily prepared in good yields from either the addition two equivalents of a neutral ligand (L) or one equivalent of a bidentate ligand (L_2) to the $[Pd(bit)_2].H_2O$ or *via* the nucleophilic displacement of chloride for benzisothiazolinate ligands in *trans*-$[PdCl_2L_2]$. Spectroscopic data and an X-ray crystal structure of *cis*-$[Pd(bit)_2(\kappa^2\text{-dppe})]$ suggest that the benzisothiazolinate ligands are bonded in a monodentate fashion through nitrogen in all cases. We are currently developing the related platinum(II) chemistry from the precursor $[Pt(bit)_2].H_2O$ and this will then allow a comparison of their biological properties with those of the closely related saccharinate and thiosaccarinate complexes which show promising anticancer activity.

Supplementary information

CCDC 1058948 contains the supplementary crystallographic data for **15**·2EtOH. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/datarequest/cif

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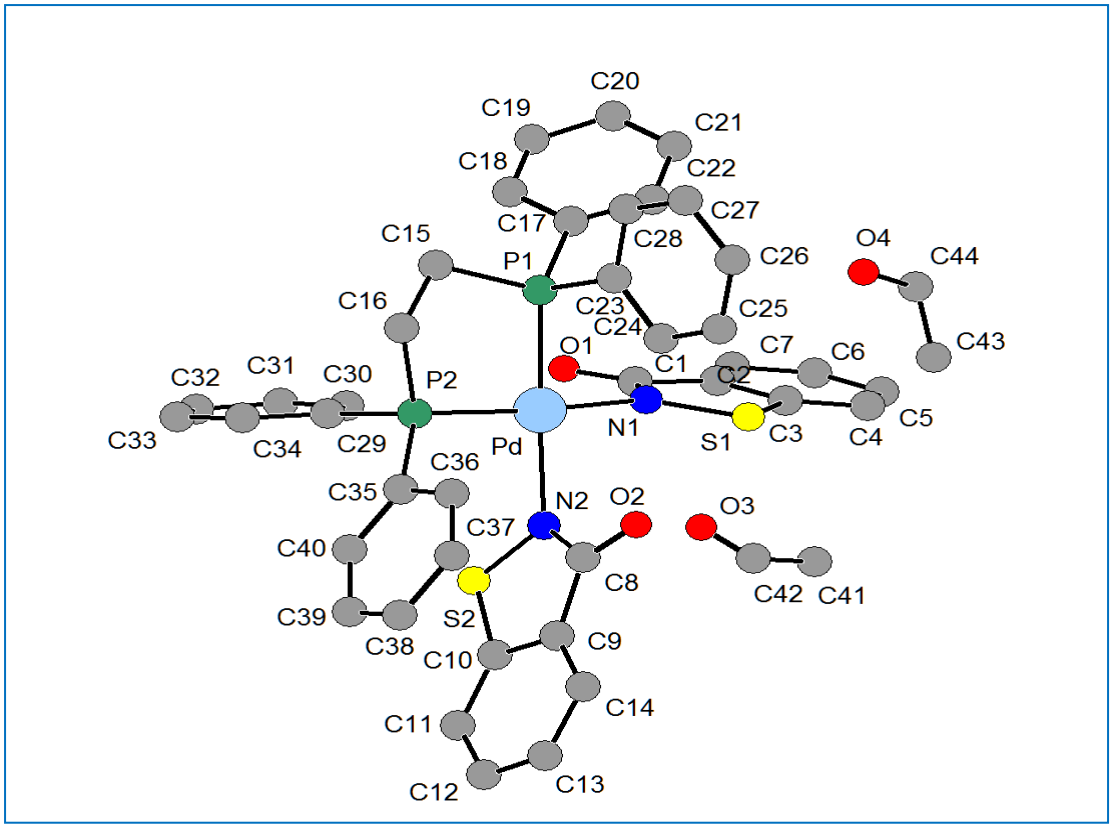

Figure 1. The molecular structure of [Pd(bit)$_2$(κ^2-dppe)].2EtOH (**15**.2EtOH) with selected bond lengths (Å) and angles (^{o}); Pd-P(1) 2.234(1), Pd-P(2) 2.230(1), Pd-N(1) 2.070(3), Pd-N(2) 2.100(3), N(1)-S(1) 1.672(3), N(2)-S(2) 1.676(3), P(1)-Pd-P(2) 84.81(4), N(1)-Pd-N(2) 92.37(11), N(1)-Pd-P(2) 172.56(9), N(2)-Pd-P(1) 168.09(10)

Table 1. Crystallographic data for $[Pd(bit)_2(\kappa^2\text{-dppe})].2EtOH$	
Empirical formula	$C_{44}\ H_{44}\ N_2\ O_4\ P_2\ Pd\ S_2$
Formula weight	897.27
Temperature	200(2) K
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, $P2_1/n$
Unit cell dimensions	a = 11.7951(8) Å, $\alpha = 90^o$
	b = 23.9615(14) Å, $\beta = 109.783(5)^o$
	c = 15.8756(12) Å, $\gamma = 90^o$
Volume	4222.1(5) $Å^3$
Z, Calculated density	4, 1.412 mg/m^3
Absorption coefficient	0.658 mm^{-1}
F(000)	1848
Crystal size	0.50 x 0.11 x 0.06 mm
Theta range for data collection	3.87 to 25.00°
Limiting indices	-14<=h<=13, -28<=k<=28, -18<=l<=18
Reflections collected / unique	21224 / 7369 [R(int) = 0.0716]
Completeness to theta = 25.00	99.3 %
Max. and min. transmission	0.9616 and 0.7344
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7369 / 7 / 545
Goodness-of-fit on F^2	0.622
Final R indices [I>2sigma(I)]	$R_1 = 0.0313$, $wR_2 = 0.0510$
R indices (all data)	$R_1 = 0.0827$, $wR_2 = 0.0558$
Largest diff. peak and hole	0.410 and -0.453 $e.A^{-3}$