Pyridine-2-thionate as a versatile ligand in Pd(II) and Pt(II) chemistry: the presence of three different co-ordination modes in $[Pd_2(\mu_2\text{-}S,N\text{-}C_5H_4SN)(\mu_2\text{-}\kappa^2S\text{-}C_5H_4SN)(\mu_2\text{-dppm})(S\text{-}C_5H_4SN)_2]$

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Reactions of $[MCl_2(L\text{–}L)]$, M = Pt, Pd; L–L = bis(diphenylphosphino)methane (dppm) or bis(diphenylphosphino)ethane (dppe), with NaC_5H_4SN in a 1 : 2 molar ratio lead to mononuclear species $[M(S\text{-}C_5H_4SN)_2(P\text{–}P)]$, M = Pt; L–L = dppm (**1**) or dppe (**2**) and M = Pd; L–L = dppe (**3**), as well as to the dinuclear $[Pd_2(\mu_2\text{-}S,N\text{-}C_5H_4SN)(\mu_2\text{-}\kappa^2S\text{-}C_5H_4SN)(\mu_2\text{-dppm})(S\text{-}C_5H_4SN)_2]$ (**4**). In contrast, reaction of $[MCl_2(dppm)]$ with NaC_5H_4SN in a 1 : 1 molar ratio leads to $[Pd_2(\mu_2\text{-}S,N\text{-}C_5H_4SN)_3(\mu_2\text{-dppm})]Cl$ (**5**) and *trans*-$[Pt(S\text{-}C_5H_4SN)_2(PPh_2Me)_2]$ (**6**) respectively. The latter is formed in low yield by cleavage of the dppm ligand. The dinuclear derivatives **4** and **5** present an A-frame and lantern structure, respectively. The former showing three different co-ordination modes in the same molecule with a short Pd–Pd distance of 2.9583 (9) Å and the latter with three bridging S,N thionate ligands showing a shorter Pd–Pd distance of 2.7291 (13) Å. Both distances could be imposed by the bridging ligands or point to some sort of metal–metal interaction.

Introduction

Compounds containing heterocyclic thione and/or thionate groups linked to one or more metallic centres have been known for several decades. However, in the last decade they have provoked more interest[1–5] due to their wide range of applications. In general, the presence of metal thiolates in biological systems,[6–8] their application as fungicides,[8,9] as electric conductors[10,11] and in the pharmaceutical industry,[9,12–14] including the anticarcinogenic properties[15,16] of some complexes with platinum and gold, have been responsible for, among other aspects, raising the interest in heterocyclic thiones and thionates as a source of sulfur donor ligands. The co-ordination chemistry of heterocyclic thiones and their corresponding anions as ligands is very rich, combining a soft and hard end which can be interesting for catalytic applications. Therefore, terminal S-bonding or N-bonding, S-bridging, N,S-chelating, N,S-bridging, N,S-chelation-cum-S-bridging or N,S-bridging-cum-S-bridging modes are found in the literature.[1–5] Structural studies show that binuclear complexes containing bridging heterocyclic thionate ligands are the most represented. However, in contrast with the large number of complexes based on two bridging ligands that have been reported, there are only two examples of three bridging co-ordination modes to date, that is, $[NaV(\mu_2\text{-}\kappa^2S,\kappa N\text{-}C_5H_4SN)_3(S,N\text{-}C_5H_4SN)(thf)_2]$[17] and $[Ru_2(\mu_2\text{-}\kappa^2S,\kappa N\text{-}C_5H_4SN)_2(\mu_2\text{-}S,N\text{-}C_5H_4SN)(S,N\text{-}C_5H_4SN)_2][CF_3SO_3]$,[18] the latter being the only reported example of coexistence of three different co-ordination modes of pyridine-2-thionate in the same complex.

With regard to the chemistry of palladium and platinum mononuclear complexes with the general formula $[M(C_5H_4SN)_2(L)_2]$ (M = Pd, Pt; L = PPh_3,[19,20] L_2 = dppe[21]), $[MCl(C_5H_4SN)(PPh_3)]$, $[M(C_5H_4SN)_2(PPh_3)]$ (M = Pd, Pt),[19] $[PdCl(C_5H_4SN)(PPh_3)_2]$[19] or $[\{PdCl(S,N)(PMe_3)\}_2]$ (S,N = C_5H_4SN,[22] $C_4H_3N_2S$, $C_4(Me)H_2SN_2$ and $C_3H_2SN(Me)N$[23]) or $[Pd(S,N)(L)_2][ClO_4]$[24] with S,N = C_5H_4SN, $C_4H_3SN_2$, $C_3H_3SN_2$, $C_3H_2SN_2CH_3$, $C_3H_2S_2N$ and L = PPh_3 or L_2 = dppe, were prepared. The procedures used are oxidative addition reaction of dipyridyl-2,2′-disulfide to $[M(PPh_3)_4]$, metathesis replacement of chlorine from $[Pd(\mu\text{-}Cl)Cl(PPh_3)]_2$, $[MCl(C_5H_4SN)(PPh_3)]$ and $[Pd(\mu\text{-}Cl)Cl(PMe_3)]_2$, and deprotonation of the corresponding thione through the μ-hydroxo anion of the precursor[24] $[\{Pd(\mu\text{-}OH)_2(L)_2\}][ClO_4]_2$.

In this paper we describe the reactions of sodium pyridine-2-thionate with $[MCl_2(L\text{–}L)]$ (M = Pd, Pt and L–L = dppm, dppe) in a 2 : 1 or 1 : 1 molar ratio showing different behaviours depending on the metal, ligand or reactive molar ratios. With dppe—independent of metal and conditions—only disubstituted $[M(C_5H_4SN)_2(dppe)]$ (**2**, **3**) complexes are obtained. However, with the dppm derivatives, complexes $[Pd_2(C_5H_4SN)_4(dppm)]$ (**4**) and $[Pd_2(C_5H_4SN)_3(dppm)]Cl$ (**5**), or $[Pt(C_5H_4SN)_2(dppm)]$ (**1**) were obtained. The X-ray structures confirm the mononuclear nature of **1** and in the case of dinuclear complexes **4** and **5** show an A-frame structure for the former and a lantern structure for the latter. In addition complex **4** shows an unprecedented combination of three different modes of co-ordination of pyridine-2-thionate in the same complex.

Experimental

Chemicals

Pyridine-2-thione (C_5H_5SN) (Aldrich), Na (Aldrich), dppm, dppe or PPh_2Me (Aldrich) were used as received. Platinum and $PdCl_2$ were procured from INCOMETAL, S.A. Reagent grade diethyl ether, hexane or dichloromethane were dried using standard

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procedures and freshly distilled immediately before use. Absolute ethanol was deoxygenated with an N_2 purge. The complexes [$PtCl_2$(dppm)], [$PtCl_2$(dppe)], [$PdCl_2$(dppm)] and [$PdCl_2$(dppe)] were prepared by adding the appropriate diphosphine ligand to a solution of [$PtCl_2$(COD)] or [$PdCl_2(NCPh)_2$]. These two reagents were prepared by literature routes or slight variations thereof.[25] All starting manipulations were carried out under a nitrogen atmosphere using Schlenk line and syringe techniques.[26]

Physical measurements

^{1}H and ^{31}P NMR spectra were recorded on a Varian Unity 300 MHz or INOVA 400 MHz for ^{1}H, and 121.4 MHz or 161.9 MHz for ^{31}P, in $CDCl_3$ or CD_2Cl_2 solutions; ^{1}H chemical shifts are quoted relative to tetramethylsilane (internal reference) and the ^{31}P NMR chemical shifts to H_3PO_4 (external reference) or to an internal reference. IR spectra were recorded on a Perkin Elmer 843 (range 4000–200 cm^{-1}) and/or a Nicolet Impact 410 FTIR (range 4000–400 cm^{-1}) spectrophotometers using Nujol mulls between polyethylene sheets. Conductivity measurements were performed at 298 K using a Crison 522 conductimeter ($c \approx 5.10^{-4}$ M). The C, H, N and S analyses were performed with a LECO CHNS 932 microanalyser. Mass spectra were recorded on a VG Autospec, by LSIMS+ using nitrobenzyl alcohol as matrix. The X-ray intensity data were collected with an Enraf Nonius Kappa CCD detector or a Bruker-Smart CCD diffractometer with graphite-monochromated Mo-Kα ($\lambda = 0.71073$ Å).

Syntheses

Preparation of [Pt(*S*-$C_5H_4SN)_2$(dppm)] (1). NaC_5H_4SN (0.390 mmol)—prepared *in situ* from NaEtO 0.1 M (3.9 mL, 0.390 mmol) and C_5H_5SN (43.4 mg, 0.390 mmol) in absolute CH_3CH_2OH (20 mL)—was added to a suspension of [$PtCl_2$-(dppm)] (127 mg, 0.195 mmol) in absolute CH_3CH_2OH (20 mL) under an inert atmosphere. A pale bright yellow solution was formed immediately and the white solid in suspension remained mixed with a pale yellow solid. After stirring for 24 h at room temperature, the solvent was removed partially to concentrate the suspension to *ca.* 5 mL. The solid was filtered off and dissolved in CH_2Cl_2 (10 mL). The yellow solution was then filtered and concentrated to *ca.* 2 mL under vacuum. Diethyl ether was added to precipitate the product followed by filtration, washing with diethyl ether and hexane to produce a pale yellow crystalline solid in 86% yield. X-Ray quality crystals were grown by slow diffusion of hexane into a CH_2Cl_2 solution of the complex. Anal. Calcd for $C_{35}H_{30}PtN_2P_2S_2$: C, 52.56; H, 3.78; N, 3.51; S, 8.00. Found: C, 52.40; H, 3.93; N, 3.43; S, 7.84%. Λ_M (Ω^{-1} cm^2 mol^{-1}): 2.18. IR (Nujol mull, cm^{-1}): (C_5H_4SN) 1573 (vs), 1545 (s). ^{1}H NMR (δ, in $CDCl_3$): 7.84 (m, 8 H, Ph), 7.41 (d, $^3J_{H6-H5} = 7.15$ Hz, 2 H, C_5H_4SN), 7.27 (m, 12 H, Ph), 7.09 (m, 2H, C_5H_4SN), 6.96 (t, $^3J_{H5-H4} = 6.88$ Hz, 2H, C_5H_4SN), 6.31 (t, $^3J_{H-H} = 6.80$ Hz, 2H, C_5H_4SN), 4.33 (t, $^2J_{H-P} = 14.7$ Hz, 2H, –CH_2–, dppm). ^{1}H{^{31}P} NMR (δ, in $CDCl_3$): 4.33 (s, $^3J_{H-Pt} = 58.1$ Hz, 2H, –CH_2–, dppm). ^{31}P{^{1}H} NMR (δ, in $CDCl_3$): −49.8 (s, $^1J_{P-Pt} = 2780.1$ Hz). MS-LSIMS+ (*m*/*z*): 689 [Pt(C_5H_4SN)(dppm)$^+$, 100%].

Preparation of [Pt(*S*-$C_5H_4SN)_2$(dppe)] (2). NaC_5H_4SN (0.386 mmol)—prepared *in situ* from NaEtO 0.1 M (3.9 mL, 0.386 mmol) and C_5H_5SN (43.0 mg, 0.386 mmol) in absolute CH_3CH_2OH (20 mL)—was added to a suspension of [$PtCl_2$(dppe)] (128.5 mg, 0.193 mmol) in absolute CH_3CH_2OH (20 mL) under an inert atmosphere. A lemon yellow solution appeared immediately and slowly became totally clear. After stirring for 5 h at room temperature, the solution was concentrated to *ca.* 5 mL under vacuum and hexane was added (20 mL). The pale yellow solid precipitate was isolated by filtration and obtained in 75% yield. Anal. Calcd for $C_{36}H_{32}PtN_2P_2S_2$: C, 53.13; H, 3.96; N, 3.44; S, 7.88. Found: C, 52.83; H, 3.81; N, 3.59; S, 7.66%. Λ_M (Ω^{-1} cm^2 mol^{-1}): 3.8. IR (Nujol mull, cm^{-1}): (C_5H_4SN) 1566 (vs), 1542 (vs). ^{1}H NMR (δ, in $CDCl_3$): 7.80 (m, 8H, Ph), 7.62 (d, $^3J_{H6-H5} = 4.87$ Hz, 2H, C_5H_4SN), 7.32 (m, 12 H, Ph), 7.26 (d, $^3J_{H3-H4} = 10.96$ Hz, 2H, C_5H_4SN), 6.84 (td, $^3J_{H4-H5} = 7.39$ Hz, $^4J_{H4-H6} = 1.93$ Hz, 2H, C_5H_4SN), 6.40 (t, $^3J_{H-H} = 7.58$ Hz, 2H, C_5H_4SN), 2.21 (d, $^2J_{H-P} = 18.17$ Hz, $^3J_{H-Pt} = 47.1$ Hz, 4H, –CH_2–, dppe). ^{31}P{^{1}H} NMR (δ, in $CDCl_3$): 46.29 (s, $^1J_{P-Pt} = 2966.29$ Hz). MS-LSIMS+ (*m*/*z*): 703 [Pt(C_5H_4SN)(dppe)$^+$, 100%].

Preparation of [Pd(*S*-$C_5H_4SN)_2$(dppe)] (3). NaC_5H_4SN (0.610 mmol)—prepared *in situ* from NaEtO 0.1 M (6.1 mL, 0.610 mmol) and C_5H_5SN (67.8 mg, 0.610 mmol) in absolute ethanol (20 mL)—was added to a suspension of [$PdCl_2$(dppe)] (175.5 mg, 0.305 mmol) in absolute ethanol (20 mL) under an inert atmosphere. A white-yellow suspension in an orange solution was formed immediately. After stirring for 24 h at room temperature, the solvent was removed under vacuum to *ca.* 5 mL and the solid filtered off. The resulting gold-yellow solid was purified by re-crystallisation from dichloromethane–hexane and **3** was isolated in 83% yield. Anal. Calcd for $C_{36}H_{32}PdN_2P_2S_2$: C, 59.63; H, 4.45; N, 3.86; S, 8.84. Found: C, 59.42; H, 4.65; N, 3.95; S, 8.97%. Λ_M (Ω^{-1} cm^2 mol^{-1}): 1.7. IR (Nujol mull, cm^{-1}): (C_5H_4SN) 1567 (vs), 1542 (vs). ^{1}H NMR (δ, in $CDCl_3$): 7.79 (m, 10H, Ph, –N–C–H–, C_5H_4SN), 7.36 (m, 12H, Ph), 7.07 (d, $^3J_{H3-H4} = 8.00$ Hz, 2H, C_5H_4SN), 6.79 (t, $^3J_{H-H} = 8.00$ Hz, 2H, C_5H_4SN), 6.44 (t, $^3J_{H-H} = 8.00$ Hz, 2H, C_5H_4SN), 2.31 (d, $^2J_{H-P} = 20.0$ Hz, 4H, –CH_2–, dppe). ^{31}P{^{1}H} NMR (δ, in $CDCl_3$): 57.7 (s). MS-LSIMS+ (*m*/*z*): 614 [Pd(C_5H_4SN)(dppe)$^+$, 100%].

Preparation of [Pd_2(μ$_2$-*S*,*N*-C_5H_4SN)(μ$_2$-κ^2*S*-C_5H_4SN)(μ$_2$-dppm)(*S*-$C_5H_4SN)_2$] (4). NaC_5H_4SN (0.390 mmol)—prepared *in situ* from NaEtO 0.1 M (3.9 mL, 0.390 mmol) and C_5H_5SN (43.4 mg, 0.390 mmol) in CH_3CH_2OH (20 mL)—was added to a suspension of [$PdCl_2$(dppm)] (127 mg, 0.195 mmol) in CH_3CH_2OH (20 mL) under an inert atmosphere. A clear orange solution appeared within 5 minutes and the resulting solution was stirred for 4 h. The solution was concentrated under vacuum to *ca.* 1 mL, dichloromethane (10 mL) was added and the solid residue filtered off. Concentration of the resulting solution to *ca.* 2 mL and addition of hexane (20 mL) led to **4** as an orange solid in 76% yield. X-Ray quality crystals were grown by slow diffusion of hexane into a CH_2Cl_2 solution of the complex. Anal. Calcd for $C_{45}H_{38}Pd_2N_4P_2S_4$: C, 52.08; H, 3.69; N, 5.39; S, 12.36. Found: C, 51.82; H, 3.65; N, 5.20; S, 12.00%. Λ_M (Ω^{-1} cm^2 mol^{-1}): 2.8. IR (Nujol mull, cm^{-1}): (C_5H_4SN) 1587 (s), 1572 (vs), 1558 (m), 1542 (s). ^{1}H NMR (δ, in $CDCl_3$): 9.39 (m, 1H, C_5H_4SN), 8.66 (m, 1H, C_5H_4SN), 8.48 (m, 1H, C_5H_4SN), 8.44 (m, 1H, C_5H_4SN), 8.23 (m, 1H, C_5H_4SN), 7.88 (m, 8H, Ph), 7.70 (m, 2H, C_5H_4SN), 7.50

(m, 2H, C_5H_4SN), 7.33 (m, 12H, Ph), 7.05 (m, 1H, C_5H_4SN), 6.92 (m, 1H, C_5H_4SN), 6.85 (m, 2H, C_5H_4SN), 6.53 (m, 1H, C_5H_4SN), 6.04 (m, 2H, C_5H_4SN), 4.36 (dt, $^2J_{H-P}$ = 11.6 Hz, 1H, –CH_2–, dppm), 4.21 (dt, $^2J_{H-P}$ = 11.6 Hz, 1H, –CH_2–, dppm). $^1H\{^{31}P\}$ NMR (δ, in $CDCl_3$): 4.40 (d, AB system, J_{AB} = 14.6 Hz, 1H, –CH_2–, dppm), 4.18 (d, AB system, J_{AB} = 14.6 Hz, 1H, –CH_2–, dppm). $^{31}P\{^1H\}$ NMR (δ, in $CDCl_3$): 33.75 (d, $^2J_{P-P}$ = 48.6 Hz), 29.15 (d, $^2J_{P-P}$ = 48.6 Hz). MS-FAB (m/z): 600 [$Pd(C_5H_4SN)(dppm)^+$, 20%], 928 [$Pd_2(C_5H_4SN)_3(dppm)^+$, 60%].

Preparation of [$Pd_2(\mu_2$-*S*,*N*-$C_5H_4SN)_3(\mu_2$-dppm)]Cl (5). NaC_5H_4SN (0.463 mmol)—prepared *in situ* from NaEtO 0.1 M (4.6 mL, 0.463 mmol) and C_5H_5SN (51.4 mg, 0.463 mmol) in absolute CH_3CH_2OH (20 mL)—was added to a suspension of [$PdCl_2$(dppm)] (259.9 mg, 0.463 mmol) in absolute CH_3CH_2OH (20 mL) under an inert atmosphere. A clear red-orange solution appeared within 5 minutes and it was stirred for 6 h. The solution was concentrated under vacuum to *ca.* 1 mL, dichloromethane (10 mL) was added and the solid residue filtered off. Concentration of the resulting solution to *ca.* 2 mL and addition of hexane (20 mL) resulted in **5** as a red-orange solid in a 63% yield. X-Ray quality crystals were grown by slow diffusion of hexane into a CH_2Cl_2 solution of the complex giving the corresponding dichloromethane and water solvate of complex **5**. Anal. Calcd for $C_{41}H_{38}Pd_2N_3OP_2S_3Cl$: C, 46.19; H, 3.59; N, 3.94; S, 9.02. Found: C, 45.93; H, 3.61; N, 3.76; S, 8.78%. Λ_M (Ω^{-1} cm^2 mol^{-1}): acetone, 46.0. IR (Nujol mull, cm^{-1}): (C_5H_4SN) 1585 (s), 1543 (m). ^1H NMR (δ, in $CDCl_3$): 9.41 (d, $^3J_{H-H}$ = 5.15 Hz, 1H, C_5H_4SN), 8.70 (d, $^3J_{H-H}$ = 5.15 Hz, 1H, C_5H_4SN), 8.48 (t, $^3J_{H-H}$ = 7.67 Hz, 2H, C_5H_4SN), 8.20 (d, $^3J_{H-H}$ = 5.77 Hz, 1H, C_5H_4SN), 8.11 (m, 2H, C_5H_4SN), 7.65 (m, 8H, Ph), 7.43 (t, $^3J_{H-H}$ = 8.06 Hz, 2H, C_5H_4SN), 7.09 (d, $^3J_{H-H}$ = 7.86 Hz, 1H, C_5H_4SN), 6.93 (m, 12H, Ph), 6.58 (dd, $^3J_{H-H}$ = 6.96 Hz, 2H, C_5H_4SN), 4.36 (dt, $^2J_{H-P}$ = 11.8 Hz, 1H, –CH_2–, dppm), 4.21 (dt, $^2J_{H-P}$ = 11.8 Hz, 1H, –CH_2–, dppm). $^1H\{^{31}P\}$ NMR (δ, in $CDCl_3$): 4.34 (d, AB system, J_{AB} = 11.7 Hz, 1H, –CH_2–, dppm), 4.21 (d, AB system, J_{AB} = 11.7 Hz, 1H, –CH_2–, dppm). $^{31}P\{^1H\}$ NMR (δ, in $CDCl_3$): 32.85 (d, $^2J_{P-P}$ = 60.8 Hz), 28.82 (d, $^2J_{P-P}$ = 60.8 Hz). MS-LSIMS+ (m/z): 490 [$Pd(dppm)^+$, 8%], 600 [$Pd(C_5H_4SN)(dppm)^+$, 40%], 708 [$Pd_2(C_5H_4SN)(dppm)^+$, 4%], 818 [$Pd_2(C_5H_4SN)_2(dppm)^+$, 8%], 928 [$Pd_2(C_5H_4SN)_3(dppm)^+$, 21%].

Preparation of *trans*-[Pt(*S*-$C_5H_4SN)_2(PPh_2Me)_2$] (6).

Method 1. Starting from NaC_5H_4SN (0.331 mmol)—prepared *in situ* from NaEtO 0.1 M (3.3 mL, 0.331 mmol) and C_5H_5SN (36.8 mg, 0.331 mmol) in absolute CH_3CH_2OH (20 mL)—and [$PtCl_2$(dppm)] (215.3 mg, 0.331 mmol) in absolute CH_3CH_2OH (20 mL) the reaction was carried out under the same conditions mentioned above for all cases. A pale bright yellow solution was formed immediately and the white suspended solid disappeared in half an hour. After stirring for 2 h at room temperature, the solvent was partially removed to concentrate the solution to *ca.* 5 mL. The pale yellow suspended solid was filtered off and dissolved in CH_2Cl_2 (10 mL). The pale yellow solution was then filtered and concentrated to *ca.* 2 mL under vacuum. Hexane (10 mL) was added to precipitate the product followed by filtration, washing with hexane to obtain a pale yellow crystalline solid in 40% yield. X-Ray quality crystals were grown by slow diffusion of hexane into a CH_2Cl_2 solution of the complex. Anal. Calcd for $C_{36}H_{34}PtN_2P_2S_2$: C, 53.00; H, 4.20; N, 3.43; S, 7.86. Found: C, 52.80; H, 4.13; N, 3.23; S, 7.64%. Λ_M (Ω^{-1} cm^2 mol^{-1}): acetone, 3.2. IR (Nujol mull, cm^{-1}): (C_5H_4SN) 1572 (vs), 1541 (s). ^1H NMR (δ, in CD_2Cl_2): 7.96 (d, $^3J_{H6-H5}$ = 5.40 Hz, 2H, C_5H_4SN), 7.60 (m, 8H, Ph), 7.26 (m, 12H, Ph), 6.99 (d, $^3J_{H3-H4}$ = 8.05 Hz, 2H, C_5H_4SN), 6.87 (td, $^3J_{H-H}$ = 7.0 Hz, $^4J_{H4-H6}$ = 1.83 Hz, 2H, C_5H_4SN), 6.63 (t, $^3J_{H5-H6}$ = 6.50 Hz, 2H, C_5H_4SN), 2.06 (t, $^2J_{H-P}$ = 3.50 Hz, $^3J_{H-Pt}$ = 24.8 Hz, 6H, –CH_3). $^1H\{^{31}P\}$ NMR (δ, in CD_2Cl_2): 2.06 (s, $^3J_{H-Pt}$ = 24.8 Hz, 6H, –CH_3). $^{31}P\{^1H\}$ NMR (δ, in CD_2Cl_2): 8.28 (s, $^1J_{P-Pt}$ = 2733.3 Hz). MS-FAB+ (m/z): 505 [$Pt(C_5H_4SN)(PPh_2Me)^+$, 33%], 705 [$Pt(C_5H_4SN)(PPh_2Me)_2^+$, 100%].

Method 2. NaC_5H_4SN (40 mg, 0.300 mmol)—prepared *in situ* from NaEtO 0.1 M (3.0 mL, 0.300 mmol) and C_5H_5SN (33.3 mg, 0.300 mmol) in absolute CH_3CH_2OH (20 mL)—was added to a suspension of [$PtCl_2(PPh_2Me)_2$] (100.0 mg, 0.150 mmol) in absolute CH_3CH_2OH (20 mL) under an inert atmosphere. A pale bright yellow solution was formed and it became totally clear in 15 minutes. After stirring for 4 h at room temperature, the solution was concentrated to *ca.* 5 mL under vacuum and the pale yellow solid precipitate was isolated by filtration, washed with absolute ethanol (3 mL) and obtained in 82% yield. It was characterised by elemental analysis and ^1H and ^{31}P NMR spectroscopies as compound **6**.

X-Ray structure determinations of 1, 4, 5 and 6

Pale yellow (**1**), orange (**4**), red-orange (**5**) and yellow (**6**) crystals, suitable for X-ray diffraction, were grown by slow diffusion of hexane into a CH_2Cl_2 solution of each product at room temperature. A crystal of each compound was mounted on a glass fibre with inert oil and centred in a Enraf Nonius Kappa CCD area detector in the case of **1**, or in a Bruker-Smart CCD diffractometer (**4**, **5** and **6**) with graphite-monochromated Mo-Kα (λ = 0.7107 Å) radiation for data collection. Semi-empirical absorption corrections based on symmetry-equivalent reflections using SORTAV[27] were applied for **1**. For structures **4**, **5** and **6**, the SADABS program was used to correct the absorption data.[28] A summary of the fundamental crystal and refinement data of the compounds is given in Table 1.

The structures were solved by direct methods using SHELXS.[29] Full-matrix least squares refinement was carried out using SHELXL minimizing $w(F_0^2 - F_c^2)^2$.[30] Weighted R factors (R_w) and all goodness-of-fit S values are based on F^2; conventional R factors (R) are based on F. In the case of **5** the dichloromethane molecule is disordered.

CCDC reference numbers 275126–275129.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b508438e

Results and discussion

The reaction of [$PtCl_2$(dppm)], [$PtCl_2$(dppe)] or [$PdCl_2$(dppe)] with an ethanolic solution of Na(C_5H_4SN) prepared *in situ* from equimolar amounts of C_5H_5SN and NaOEt in ethanol in a 1 : 2 molar ratio afforded complexes **1**, **2** or **3**, respectively, in good yields.

M = Pt L–L = dppm (**1**); dppe (**2**)

M = Pd L–L = dppe (**3**)

Table 1 Crystallographic data for **1**, **4**, **5** and **6**

	1	**4**	**5**	**6**
Empirical formula	$C_{35}H_{30}N_2P_2PtS_2$	$C_{45}H_{38}N_4P_2Pd_2S_4$	$C_{41}H_{38}Cl_3N_3OP_2Pd_2S_3$	$C_{36}H_{34}N_2P_2PtS_2$
M	799.76	1037.77	1066.01	815.80
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_12_12_1$	$P2_1/c$	$C2/c$	$P2_1/n$
Z	4	4	8	2
a/Å	8.577(2)	20.508(4)	17.593(4)	8.8507(18)
b/Å	15.228(3)	9.0092(18)	16.091(3)	12.027(2)
c/Å	23.913(5)	25.545(5)	32.380(7)	15.874(3)
α/°	90.00	90.00	90.00	90.00
β/°	90.00	112.66(3)	93.58(3)	102.75(3)
γ/°	90.00	90.00	90.00	90.00
V/Å^3	3123.3(12)	4355.6(15)	9149(3)	1648.1(6)
ρ_{calcd}/g cm^{-3}	1.701	1.583	1.548	1.644
Crystal dimensions/mm	0.3 × 0.25 × 0.25	0.55 × 0.40 × 0.30	0.40 × 0.25 × 0.35	0.15 × 0.10 × 0.10
T/K	150(2)	293(2)	293(2)	293(2)
No. of obsd data ($I > 2\sigma(I)$)	7142	10779	4272	4084
R(int)	0.0616	0.0691	0.0463	0.0470
No. of parameters varied	379	516	502	197
μ/cm^{-1}	47.57	11.28	12.000	44.63
$R1$ (F_o)[a], $wR2$(F_o^2)[b] ($I > 2\sigma(I)$)	0.0277, 0.0632	0.0443, 0.0806	0.0515, 0.1532	0.0264, 0.0447
$R1$(F_o), $wR2$(F_o^2) (all data)	0.0308, 0.0647	0.0966, 0.0949	0.0633, 0.1607	0.0538, 0.0494

[a] $R1 = \Sigma\,||F_o| - |F_c||/\Sigma\,|F_o|$. [b] $wR2 = \{\Sigma w[|F_o|^2 - |F_c|^2]^2/\Sigma w(F_o^2)^2\}^{1/2}$.

$$[MCl_2(L\text{–}L)] + 2\ NaC_5H_4SN \rightarrow [M(S\text{–}C_5H_4SN)_2(L\text{–}L)] + 2\ NaCl \quad (1)$$

The reaction pathway used by us can be considered as a slight modification of the one previously described[21] to prepare compounds [Pt(*S*-$C_5H_4SN)_2$(dppe)] (**2**) or [Pd(*S*-$C_5H_4SN)_2$(dppe)] (**3**) starting from $PtCl_4$ or $PdCl_2$ and diphosphine ligand with C_5H_5SN and Et_3N as deprotonating agent. The spectroscopic data for **2** and **3** agree with those previously described[21] for the mononuclear complexes although, in the case of complex **2**, additional spectroscopic data are available in the Experimental section. Complex [Pt(*S*-$C_5H_4SN)_2$(dppm)] **1** shows a single resonance at $\delta = -49.8$ ppm in the $^{31}P\{^1H\}$ NMR spectrum in $CDCl_3$ which agree with a chelating behaviour of the diphosphine ligand.[31] The presence of only a pair of platinum satellites, $^1J_{P\text{–}Pt} = 2780.1$ Hz, point to a mononuclear structure of **1** similarly to those reported for complexes **2** and **3**.

Crystals of **1** suitable for X-ray diffraction were grown by slow diffusion of hexane into a CH_2Cl_2 solution of the complex. An ORTEP representation of **1** is shown in Fig. 1 and selected bond distances and angles for the structure are given in Table 2. The molecular structure of **1** shows two pyridine-2-thionate ligands

Table 2 Bond lengths [Å] and angles [°] for [Pt(*S*-$C_5H_4SN)_2$(dppm)] (**1**)

Pt(1)–P(1)	2.2702(11)	N(1)–C(2)	1.336(5)
Pt(1)–P(2)	2.2725(11)	S(2)–C(2)	1.761(4)
Pt(1)–S(1)	2.3358(11)	S(1)–C(7)	1.748(4)
Pt(1)–S(2)	2.3381(11)	N(2)–C(7)	1.333(5)
P(1)–Pt(1)–P(2)	74.01(4)	C(1)–P(1)–Pt(1)	94.27(12)
P(1)–Pt(1)–S(1)	102.25(4)	C(21)–P(2)–Pt(1)	116.97(14)
P(2)–Pt(1)–S(1)	174.66(4)	C(31)–P(2)–Pt(1)	124.31(14)
P(1)–Pt(1)–S(2)	179.16(4)	C(1)–P(2)–Pt(1)	94.40(13)
P(2)–Pt(1)–S(2)	105.19(4)	C(7)–S(1)–Pt(1)	112.72(14)
S(1)–Pt(1)–S(2)	78.56(4)	C(2)–S(2)–Pt(1)	114.89(14)
C(51)–P(1)–Pt(1)	115.73(14)	S(2)–C(2)–N(1)	120.7(3)
C(41)–P(1)–Pt(1)	121.80(13)	S(1)–C(7)–N(2)	120.8(3)

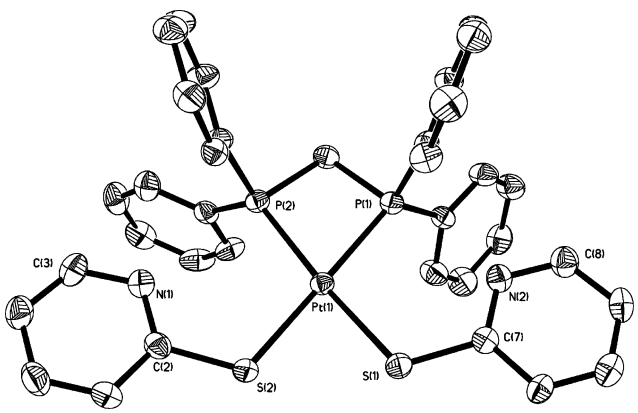
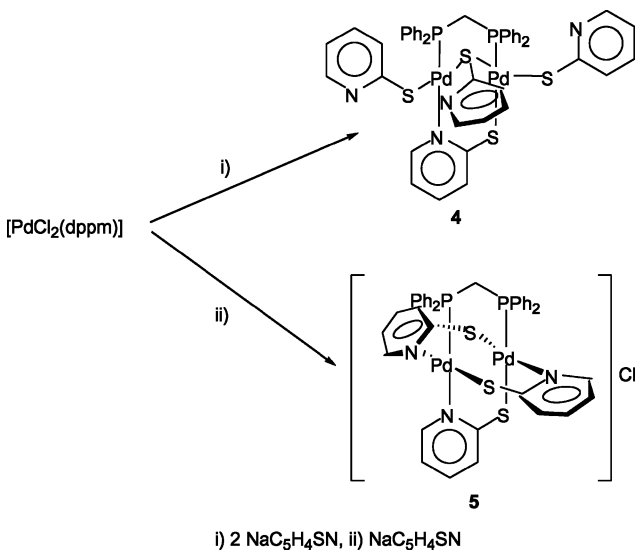


Fig. 1 Molecular structure of complex **1**. Thermal ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

in a *syn* configuration with a dihedral angle of about 45° with the PtS_2P_2 plane. The geometry around the platinum atom can be considered distorted square-planar. The main distortion arises from the closing of the P(2)–Pt–P(1) and S(2)–Pt-S(1) angles [74.01(4)° and 78.56(4)° respectively], and the opening of the S(2)–Pt-P(2) and S(1)–Pt-P(1) angles [105.19(4)° and 102.25(4)° respectively] most likely imposed by the small bite angle of the bis(diphenylphosphino)methane ligand. The phenyl groups in the dppm ligand are in an up/down configuration on either side of the PtS_2P_2 plane, which precludes the presence of short Pt–Pt intramolecular interactions in the crystal lattice. Referenced structures of [Pt(*S*-$C_5H_4SN)_2$(dppx)] (dppx = dppe, dppn, dppp)[21] and [Pt(*S*-$C_5H_4SN)_2$(bpy)][32] exhibit a difference in the orientation of the pyridine-2-thionate ligands. Pt–P distances of 2.2725(11) and 2.2702(11) Å are in the range of other mononuclear platinum derivatives with dppm as chelating ligand: [Pt(L)$_2$(dppm)] (L = CH_2Cl,[33] SePh,[34] SPh[35]). The Pt–S bond distances are 2.3358(11) and 2.3381(11) Å, which are in the range of other Pt derivatives

with terminal pyridine-2-thiolate ligands.[20,21,32] These P–Pt and Pt–S bond distances are similar to those found in compound **2**; 2.270(3), 2.256(3) Å and 2.327(3), 2.389(3) Å respectively.[21] The N–C–S angles of 120.7(3) and 120.8(3) in complex **1** are certainly close to the ideal angle for sp^2 carbons (trigonal angles) and are characteristic of a (S-C_5H_4SN) monodentate moiety.[20,36] These angles are 119.8(8)° and 114.7(9)° in compound **2** and 120.4(6)° and 114.7(6)° in compound **3**.

On the contrary, the reaction of $[PdCl_2(dppm)]$ with thionate salts under similar conditions to those reported above shows a totally different result. Therefore, the final compound of this reaction (Scheme 1, i)) has a stoichiometry $[Pd_2(C_5H_4SN)_4(dppm)]$ (**4**) deduced from elemental analyses, mass spectra (LSIMS+) and the integration of resonances in the ^1H NMR spectrum.



Scheme 1

Mass spectroscopy shows a signal assignable to the fragment $[Pd_2(C_5H_4SN)_3(dppm)]^+$, m/z 928, 60% in accordance with the proposed stoichiometry by loss of one C_5H_4SN unit. The $^{31}P\{^1H\}$ NMR spectrum shows two doublets at 33.75 and 29.15 ppm, $^2J_{P\text{-}P} = 48.6$ Hz, indicative of non-chelating dppm co-ordination and the non-equivalence of the two P ends. The ^1H NMR shows a complicated pattern in the phenyl region indicative of different modes of co-ordination of the thionate ligands and also an illustrative methylene resonance. The CH_2 protons appear as two doublets of triplets with some modifications of the intensities. $^1H\{^{31}P\}$ NMR spectroscopy simplified these signals into an AB system, $\delta_A = 4.36$, $\delta_B = 4.21$, $J_{AB} = 14.6$ Hz which allows the measurement of $J_{H\text{-}P} = 11.6$ Hz in the original spectrum.

Fortunately crystals suitable for X-ray diffraction studies were grown. The structure of **4** (Fig. 2) displays a binuclear palladium A-frame derivative, where both metallic centres show a slightly distorted square-planar geometry. Selected bond distances and angles are given in Table 3. The molecule contains four pyridine-2-thionate ligands in 3 different co-ordination modes: two of them in a terminal S-monodentate arrangement, the other two as bridging ligands in two different modes. A μ_2-S,N and other μ_2-κ^2S. This bridging combination has only been observed previously in the $[\{Rh(\mu\text{-}C_5H_4SN)(tfbb)\}_2]$ (tfbb = tetrafluorobenzobarrelene) dimer species[37] and three differing co-ordination modes in one

Table 3 Bond lengths [Å] and angles [°] for $[Pd_2(\mu_2\text{-}S,N\text{-}C_5H_4SN)(\mu_2\text{-}\kappa^2S\text{-}C_5H_4SN)(\mu_2\text{-dppm})(S\text{-}C_5H_4SN)_2]$ (**4**)

Pd(1)–P(2)	2.2837(11)	Pd(2)–S(4)	2.3453(10)
Pd(1)–S(2)	2.3262(12)	S(1)–C(2)	1.754(4)
Pd(1)–S(3)	2.3515(11)	N(1)–C(2)	1.343(5)
Pd(1)–S(4)	2.3548(11)	S(2)–C(7)	1.741(5)
Pd(1)–Pd(2)	2.9584(9)	S(3)–C(12)	1.742(4)
Pd(2)–N(3)	2.098(3)	N(3)–C(12)	1.352(5)
Pd(2)–P(1)	2.2573(11)	S(4)–C(17)	1.790(4)
Pd(2)–S(1)	2.3361(11)	N(4)–C(17)	1.325(5)
P(2)–Pd(1)–S(2)	98.94(5)	S(4)–Pd(2)–Pd(1)	51.14(3)
P(2)–Pd(1)–S(3)	177.32(4)	C(28)–P(1)–Pd(2)	112.77(13)
S(2)–Pd(1)–S(3)	82.25(5)	C(22)–P(1)–Pd(2)	116.33(12)
P(2)–Pd(1)–S(4)	82.39(4)	C(1)–P(1)–Pd(2)	114.38(12)
S(2)–Pd(1)–S(4)	178.08(4)	C(34)–P(2)–Pd(1)	123.73(13)
S(3)–Pd(1)–S(4)	96.36(4)	C(40)–P(2)–Pd(1)	114.01(12)
P(2)–Pd(1)–Pd(2)	98.66(3)	C(1)–P(2)–Pd(1)	106.32(12)
S(2)–Pd(1)–Pd(2)	127.43(4)	C(2)–S(1)–Pd(2)	103.51(14)
S(3)–Pd(1)–Pd(2)	78.74(3)	C(7)–S(2)–Pd(1)	105.79(17)
S(4)–Pd(1)–Pd(2)	50.85(3)	C(17)–S(4)–Pd(2)	112.03(12)
N(3)–Pd(2)–P(1)	172.63(9)	C(17)–S(4)–Pd(1)	107.23(13)
N(3)–Pd(2)–S(1)	92.05(9)	Pd(2)–S(4)–Pd(1)	78.02(4)
P(1)–Pd(2)–S(1)	86.84(4)	C(12)–S(3)–Pd(1)	115.28(14)
N(3)–Pd(2)–S(4)	90.78(9)	C(16)–N(3)–Pd(2)	120.0(3)
P(1)–Pd(2)–S(4)	91.13(4)	C(12)–N(3)–Pd(2)	120.2(3)
S(1)–Pd(2)–S(4)	173.16(4)	N(1)–C(2)–S(1)	115.0(3)
N(3)–Pd(2)–Pd(1)	93.34(9)	N(2)–C(7)–S(2)	119.2(3)
P(1)–Pd(2)–Pd(1)	82.35(4)	N(3)–C(12)–S(3)	123.7(3)
S(1)–Pd(2)–Pd(1)	134.81(3)	N(4)–C(17)–S(4)	116.1(3)

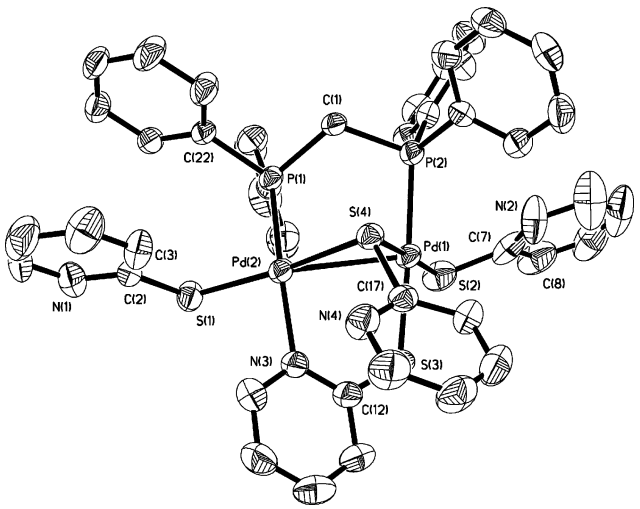


Fig. 2 Molecular structure of complex **4**. Thermal ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

compound has no precedent in the literature. The two pyridine-2-thionate groups in terminal position are *trans* to the S bridging atom, angles S(1)–Pd(2)–S(4) and S(2)–Pd(1)–S(4) being 173.16(4)° and 178.08(4)° respectively. Both groups lie almost perpendicular to the Pd_2P_2NS plane, presumably in order to minimise repulsions between these rings and the phenyl rings of the dppm ligand. The Pd–Pd distance of 2.9584(9) Å is intermediate between that found for dimers such as $[Pd_2Br_2(dppm)_2]$ 2.603 Å[38] and $[Pd_2(C_5H_4SN)_4]\cdot 2CHCl_3$ 2.677(1) Å,[39] with a direct Pd–Pd bond in the former, and the distances in the A-frame lacking a direct Pd–Pd bond (range 3.01–3.3 Å).[40,41] The presence of three co-ordination modes allows us to underscore the different angles in monodentate *S*-pyridin-2-thionate N(1)–C(2)–S(1) 115.0(3)°, N(2)–C(7)–S(2)

119.2(3)°, μ_2-κ^2S-bridging N(4)–C(17)–S(4) 116.1(3)° or μ_2-*S*,*N*-bridging N(3)–C(12)–S(3) 123.7(3)° compared with 120.6(1)° in pyridine-2-thione.[3] Regarding the S–C distances they range from 1.742(4) to 1.790(4) Å. The shorter corresponds to μ_2-*S*,*N* co-ordination and the larger to the μ_2-κ^2S co-ordination mode. This behaviour could be due to a larger electronic demand from the sulfur atom in the latter. The Pd(2)–N(3) distance of 2.098(3) Å is in the range of other similar compounds where the pyridine-2-thionate acts as chelating ligand.[22,39] However, the Pd–S and Pd–P bond lengths are slightly longer than those found in the above mentioned dimers and dppm A-frame derivatives.

When the reaction is conducted in a 1 : 1 molar ratio (Scheme 1, ii) a different complex **5** can be obtained as the main component of the reaction, which can be re-crystallised from dichloromethane/hexane. The stoichiometry of complex **5** $[Pd_2(C_5H_4SN)_3$ (dppm)]Cl is similar to complex **4** with the replacement of one thionate group by a chlorine atom as evidenced by elemental analyses and the mass spectrum which shows fragments at $[Pd_2(C_5H_4SN)_3(dppm)]^+$, *m*/*z* 928, 21%, $[Pd_2(C_5H_4SN)_2(dppm)]^+$, *m*/*z* 818, 8% and $[Pd_2(C_5H_4SN)(dppm)]^+$, *m*/*z* 708, 4% in accordance with the proposed stoichiometry by successive loss of Cl and C_5H_4SN units.

The $^{31}P\{^1H\}$ NMR spectrum shows two doublets at 32.85 and 28.82 ppm, $^2J_{P\text{-}P} = 60.8$ Hz, characteristic of a non-symmetric bidentate bridging dppm ligand. Also, the ^1H NMR is very similar to the previous complex **4** except in the less complicated phenyl region and the intensity of the signals. The integration gives a dppm/thionate ratio of 1 : 3. The methylene region shows a doublet of doublets of triplets resolved into an AB system [$^1H\{^{31}P\}$ NMR, $\delta_A = 4.36$, $\delta_B = 4.21$, $J_{AB} = 11.7$ Hz] which allowed us to measure $^2J_{H\text{-}P} = 11.8$ Hz. This spectrum, which does not change substantially down to the lowest temperature (−55 °C) accessible in $CDCl_3$, points to a structure for complex **5** similar to those reported for complex **4**. Only the conductivity in acetone (46 Ω^{-1} cm^2 mol^{-1}), which is intermediate between non-conducting and 1 : 1 electrolyte, does not agree with this proposition. This is the reason why the X-ray structure of this complex was undertaken.

An ORTEP representation of the cationic species of **5** is shown in Fig. 3 and selected bond distances and angles for the structure are given in Table 4. The crystalline structure of the dichloromethane and water solvate of complex **5** consists of a chlorine salt where the cation is a dinuclear lantern-type palladium derivative with three pyridine-2-thionate ligands and one dppm acting as bridging ligands. Both palladium centres display a slightly distorted square-planar geometry. The two pyridine-2-thionate ligands in the equatorial position are sloping towards the third pyridine thionate (the one *trans* to the dppm ligand). The Pd–Pd distance (2.7288(12) Å) is comparable to that in $[Pd_2(\mu\text{-}C_5H_5NS)_4]$ (2.677(1) Å)[39] and $[Pd_2(\mu\text{-bttz})_4]$ (2.745(1) Å)[42] (bttz = 1,3-benzothiazole-2-thiolate), but significantly longer than those in $[Pd_2(mhp)_4]$ (2.546(1)–2.559(3) Å)[43,44] (mhp = 6-methyl-2-hydroxypyridinate), $[Pd_2(chp)_4]$ (2.567(2) Å) (chp = 6-chloro-2-hydroxypyridinate)[44] and $[Pd_2(\mu\text{-dpb})_4]$ (2.576(1) Å)[45] (dpb = *N*,*N*′-diphenylbenzamidine) and slightly shorter than in palladium metal.[46] Again in this complex a short Pd–Pd distance is indicative of some metal–metal interaction and is probably imposed in this complex by the presence of the four bridging ligands. The Pd–S, Pd–N and Pd–P bond lengths are similar to those found in complex **4**. The N–C–S angles of the μ_2-*S*,*N* pyridine-2-thionate ligands are 122.0(8)°, 123.4(6)° and 121.5(7)°, which are wider than in the other co-ordination modes of pyridine-2-thionate reported in this work. The N(2)–C(7)–S(2) angle of 123.4(6)° is close to the μ_2-*S*,*N* ligand in **4**, 123.7(3)°, although does not correspond to the μ_2-*S*,*N* pyridine-2-thionate ligand *trans* to dppm.

This different behaviour of $[PdCl_2(dppm)]$ using a 1 : 1 or 1 : 2 NaC_5H_4SN molar ratio prompted us to test the reaction of $[PtCl_2(dppm)]$ and $[MCl_2(dppe)]$ (M = Pd, Pt) with a 1 : 1 molar ratio of NaC_5H_4SN. When $[MCl_2(dppe)]$ (M = Pd, Pt) is used under these conditions only complexes **2** and **3** are obtained

Table 4 Bond lengths [Å] and angles [°] for $[Pd_2(\mu_2\text{-}S,N\text{-}C_5H_4SN)_3(\mu_2\text{-dppm})]Cl\cdot CH_2Cl_2\cdot H_2O$ (**5**)

Pd(1)–N(1)	2.081(8)	Pd(2)–P(2)	2.289(3)
Pd(1)–N(3)	2.128(7)	Pd(2)–S(1)	2.305(3)
Pd(1)–P(1)	2.266(3)	Pd(2)–S(3)	2.355(3)
Pd(1)–S(2)	2.296(2)	S(1)–C(2)	1.780(12)
Pd(1)–Pd(2)	2.7288(12)	S(2)–C(7)	1.762(9)
Pd(2)–N(2)	2.089(7)	S(3)–C(12)	1.768(11)
N(1)–Pd(1)–N(3)	92.3(3)	S(3)–Pd(2)–Pd(1)	86.34(7)
N(1)–Pd(1)–P(1)	94.0(2)	C(2)–S(1)–Pd(2)	107.4(4)
N(3)–Pd(1)–P(1)	173.2(2)	C(7)–S(2)–Pd(1)	105.5(3)
N(1)–Pd(1)–S(2)	175.1(3)	C(12)–S(3)–Pd(2)	104.0(3)
N(3)–Pd(1)–S(2)	88.6(2)	C(21)–P(1)–Pd(1)	113.4(3)
P(1)–Pd(1)–S(2)	85.33(9)	C(31)–P(1)–Pd(1)	114.1(4)
N(1)–Pd(1)–Pd(2)	90.5(2)	C(1)–P(1)–Pd(1)	114.1(3)
N(3)–Pd(1)–Pd(2)	87.8(2)	C(41)–P(2)–Pd(2)	114.5(4)
P(1)–Pd(1)–Pd(2)	94.82(7)	C(51)–P(2)–Pd(2)	115.8(3)
S(2)–Pd(1)–Pd(2)	84.81(7)	C(1)–P(2)–Pd(2)	111.2(3)
N(2)–Pd(2)–P(2)	94.4(2)	C(2)–N(1)–Pd(1)	122.8(7)
N(2)–Pd(2)–S(1)	175.9(2)	C(6)–N(1)–Pd(1)	118.7(7)
P(2)–Pd(2)–S(1)	86.52(10)	C(7)–N(2)–Pd(2)	120.8(6)
N(2)–Pd(2)–S(3)	89.5(2)	C(11)–N(2)–Pd(2)	119.9(6)
P(2)–Pd(2)–S(3)	176.10(9)	C(16)–N(3)–Pd(1)	116.0(7)
S(1)–Pd(2)–S(3)	89.61(10)	C(12)–N(3)–Pd(1)	124.5(6)
N(2)–Pd(2)–Pd(1)	90.3(2)	N(1)–C(2)–S(1)	122.0(8)
P(2)–Pd(2)–Pd(1)	93.83(7)	N(2)–C(7)–S(2)	123.4(6)
S(1)–Pd(2)–Pd(1)	85.56(7)	N(3)–C(12)–S(3)	121.5(7)

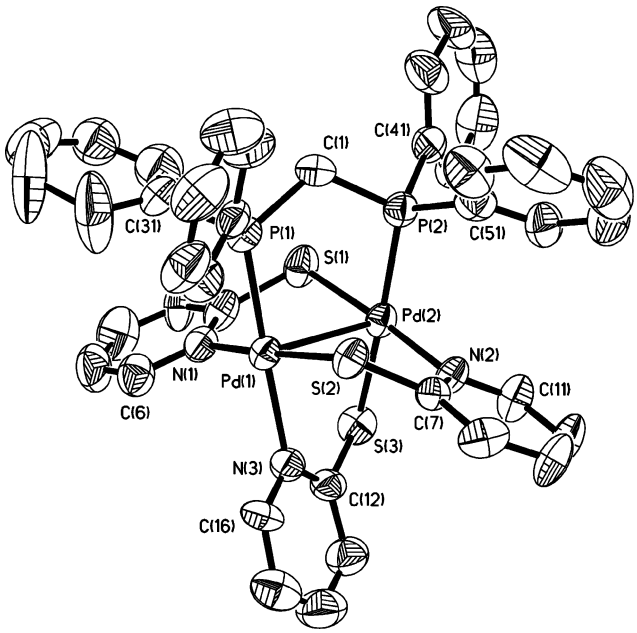


Fig. 3 The structure of the cation of complex **5**. Thermal ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

with some unreacted starting materials. However, the reaction of $[PtCl_2(dppm)]$ with NaC_5H_4SN in a 1 : 1 molar ratio affords a small quantity of an insoluble derivative in ethanol, **6**, which elemental analyses, mass spectra and NMR data surprisingly identify as $[Pt(C_5H_4SN)_2(PPh_2Me)_2]$. Complex **6** was obtained in 40% yield based on platinum. In the mother liquor of the reaction $[Pt(C_5H_4SN)_2(dppm)]$ **1** can be identified as an important component among other phosphine containing materials, which in ours hands can not be separated.

Complex **6** shows a singlet at 8.28 ppm in the $^{31}P\{^1H\}$ NMR in CD_2Cl_2 with only one set of platinum satellites, $^1J_{P\text{-}Pt} = 2733.3$ Hz, which does not seem to belong to a dppm ligand. The ^1H NMR agrees with the presence of a thionate ligand and, what is even more remarkable, is the presence of a pseudo-triplet signal at 2.06 ppm, with small $^2J_{H\text{-}P} = 3.5$ Hz, that changes to a singlet with two satellites when the $^1H\{^{31}P\}$ NMR spectrum was registered. The triplet at 2.06 ppm should correspond to the methyl groups of the two PPh_2Me ligands in *trans* positions, by virtual coupling. The LSIMS+ mass spectrum points in a similar direction showing fragments at *m/z* (%) 505 (33) and 705 (100) assignable to $[Pt(C_5H_4SN)(PPh_2Me)]^+$, and $[Pt(C_5H_4SN)(PPh_2Me)_2]^+$, respectively

The X-ray structure of one crystal of this compound has been resolved. An ORTEP representation of *trans*-$[Pt(S\text{-}C_5H_4SN)_2(PPh_2Me)_2]$ (**6**) is shown in Fig. 4 and selected bond distances and angles for the structure are given in Table 5. The molecule consists of a centrosymmetric monomer with two methyl diphenyl phosphine molecules and two pyridine-2-thionate ligands, mutually *trans*. The metallic centre shows a slightly distorted square planar geometry. This structure is analogous to the previously reported *trans*-$[Pt(C_5H_4NS)_2(PPh_3)_2]$[20] although with an elongation in the Pt–P bond lengths, being 2.3149(11) Å in **6** and 2.295 and 2.253 Å in the reported derivative. In contrast, they are shorter than in the *trans*-$[PdCl_2(PPh_2Me)_2]$[47] distances Pd–P 2.3306 Å. It is not possible to compare **6** with the *trans*-dichlorobis(methyldiphenylphosphine)platinum(II) because only the *cis* isomer is referenced in the literature.[48] The Pt–S distances are in the range of platinum pyridin-2-thionate complexes.[20,21,32]

Complex *trans*-$[Pt(S\text{-}C_5H_4SN)_2(PPh_2Me)_2]$ (**6**) can be obtained in higher yield (82%) by addition of NaC_5H_4SN in a 2 : 1 molar ratio, under an inert atmosphere, to a suspension of $[PtCl_2(PPh_2Me)_2]$ in absolute ethanol. The complex obtained this way shows identical spectroscopic properties to those of the one described above, showing that the presence of the PPh_2Me ligand comes from a cleavage of the dppm ligand. There are a few references in the literature to P–C bond cleavage in platinum complexes containing bis(diphenylphosphino)methane. In some cases, the cleavage occurs under basic phase transference catalyst (PTC) conditions in which a dppm ligand is hydrolysed to produce PPh_2Me and other fragments,[49] and the formation of *trans*-$[Pt_2(\mu_2\text{-}OH)_2(POPh_2)_2(PPh_2Me)_2]$ from $[PtCl_2(dppm)]$ are also referenced.[50] Other photochemical or thermal transformation of the dppm chelate ring have been reported.[51,52] We are currently doing some research work on this complex to understand the mechanism of this transformation, the first step of which could be the replacement of one chlorine atom with the pyridin-2-thionate ligand. Attempts to increase the yield of **6** by adding one free dppm to the reaction mixture failed giving similar results. Although in this case we were not able to isolate the other components of the reaction, essential to propose a mechanism; we are working with other heterocyclic thionate ligands to contribute more data to this reaction process.

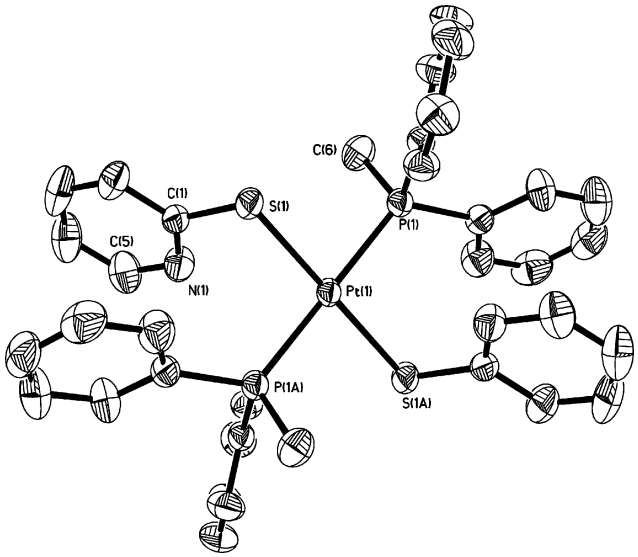


Fig. 4 Molecular structure of complex **6**. Thermal ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

Table 5 Bond lengths [Å] and angles [°] for *trans*-$[Pt(S\text{-}C_5H_4SN)_2(PPh_2Me)_2]$ (**6**)

Pt(1)–P(1)A	2.3149(11)	Pt(1)–S(1)	2.3435(9)
Pt(1)–P(1)	2.3149(11)	N(1)–C(1)	1.330(4)
Pt(1)–S(1)A	2.3435(9)	S(1)–C(1)	1.752(4)
P(1)A–Pt(1)–P(1)	180.00(5)	C(1)–S(1)–Pt(1)	106.50(12)
P(1)A–Pt(1)–S(1)A	85.12(3)	C(11)–P(1)–Pt(1)	111.08(11)
P(1)–Pt(1)–S(1)A	94.88(3)	C(6)–P(1)–Pt(1)	110.72(13)
P(1)A–Pt(1)–S(1)	94.88(3)	C(21)–P(1)–Pt(1)	121.24(11)
P(1)–Pt(1)–S(1)	85.12(3)	S(1)–C(1)–N(1)	120.3(2)
S(1)A–Pt(1)–S(1)	180.00(6)		

Symmetry transformations used to generate equivalent atoms: A $-x + 2$, $-y$, $-z + 2$.

Conclusions

In conclusion we have shown how the reactions of pyridine-2-thionate with $[MCl_2(dppm)]$ (M = Pd or Pt) depend greatly on the ratio of thionate ligand used. In fact, with palladium we have shown here two rare examples of dinuclear complexes with three $[Pd_2(\mu_2\text{-}S,N\text{-}C_5H_4SN)_3(\mu_2\text{-dppm})]Cl$ (**5**) and four $[Pd_2(\mu_2\text{-}S,N\text{-}C_5H_4SN)(\mu_2\text{-}\kappa^2S\text{-}C_5H_4SN)(\mu_2\text{-dppm})(S\text{-}C_5H_4SN)_2]$ (**4**) thionate ligands in the molecule and, in the case of **4**, the unprecedented existence of three different modes of co-ordination in the same molecule, that is: monodentate *S*-, μ_2-*S*,*N* and μ_2-κ^2*S*. The comparison of the two structures with three and two thionate bridging ligands, respectively, shows how the Pd–Pd distance is modified from 2.7291(13) to 2.9583(9) Å, which should be imposed by the bridging μ_2-*S*,*N* ligands. In contrast, the chemistry of platinum derivative $[PtCl_2(dppm)]$ affords mononuclear materials.

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