

Dalton Transactions

An international journal of inorganic chemistry

rsc.li/dalton



ISSN 1477-9226





PAPER

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Cite this: *Dalton Trans.*, 2024, **53**, 9680

Reactivity of Schiff base-[C,N,S] pincer palladacycles: hydrolysis renders singular trinuclear, tetranuclear, and heteropentanuclear Pd₃W₂ coordinated complexes†

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Treatment of the Schiff base ligands **a–f** with Li₂[PdCl₄]/NaAcO in methanol under reflux gave the single nuclear palladacycles **1a–1f**, with the metal atom bonded to a terdentate monoanionic [C,N,S] iminic ligand and to a chloride ligand that completes the palladium coordination sphere. Reaction of **1a–1c** with silver perchlorate/triphenylphosphine in acetone at room temperature yielded the single nuclear complexes **2a–2c** as the perchlorate salts, after substitution of the chloride ligand by a triphenylphosphine. However, reaction of **a–c** with Na₂[PdCl₄]/NaAcO in methanol at room temperature also gave compounds **1a–1c** albeit contaminated with small amounts of the corresponding free aldehyde (mixture A). Reaction of mixture A with silver perchlorate/triphenylphosphine in acetone at room temperature gave analogously **2a–2c** with some of the corresponding free aldehyde (mixture B). Attempts to purify mixtures A and B *via* recrystallization produced single crystals of **5** and **6** respectively: two serendipitously formed complexes, bearing thiomethyl aniline and/or acetate ligands, and void of aldehyde or iminic residue; the structures contain eight- and six-membered rings of alternating palladium and nitrogen atoms, respectively. To clarify this situation the aniline itself was reacted with palladium(II) acetate or with Na₂[PdCl₄]; in the latter case after recrystallization a unique behavior is revealed, giving rise to a tetranuclear complex containing a Pd₄N₄ ring with three differing coordination environments on the palladium atoms. Treatment of **1d** with Ph₂PCH₂PPh₂ (dppm)/AgClO₄ or with Ph₂PCH₂(PPh₂)W(CO)₅/AgClO₄ gave **3d**, with a mono-coordinated dppm ligand, and **4d**, respectively; complex **3d** could not be converted into **4d** by reaction with W(CO)₅(THF). Recrystallization of **4d** gave a still further noticeable species, complex **8**: a pentanuclear *trans*-configured heterometallic mixed valent Pd(II)/W(O) linear complex with the palladium atoms supported by two acetate and two thiomethyl aniline bridging ligands. The complexes were fully characterized by microanalysis, IR, ¹H, and ³¹P NMR spectroscopies, as appropriate. The X-ray single-crystal analyses for compounds **1b**, **5**, **6**, **7** and **8** are described.

Received 13th March 2024,

Accepted 12th April 2024

DOI: 10.1039/d4dt00756e

rsc.li/dalton

Introduction

The chemistry of palladacycles,^{1,2} first reported by Cope and Siekman,³ constitutes a flourishing part of organometallics that has attracted much research interest in past years attributable to a great extent to their versatile structural and reactivity features, mainly derived from the fact that their properties can be easily tuned, for example by modification of the cyclometalated ligand or the ancillary ligands at the metal. They are also

well known for their broad applications⁴ in numerous fields such as in organic synthesis,^{5,6} photochemistry,^{7,8} optical resolution processes,⁹ and catalysis, which after the pioneering work by Herrmann *et al.*,^{10,11} continues to be researched,^{12–21} as potential biologically active materials,^{22–31} and liquid crystals.^{32–34}

In the past we have shown that thiosemicarbazones yield palladacycles with the ligand in a terdentate [C,N,S] fashion³⁵ with formation of tetranuclear compounds possessing two distinct palladium–sulfur bonds, *i.e.*, Pd–S_{chelating} and Pd–S_{bridging}, with the ligand in a pincer mode; Kawamoto *et al.*³⁶ have reported similar structures for Schiff base [C,N,S] Pd(II) and Pt(II) complexes. This results in three strong bonds at the metal, namely the Pd–C, Pd–N and Pd–S_{chelating} bonds pertaining to two fused five-membered rings, that maintain the metal tightly bonded so that only one of the four coordination sites in the

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† CCDC 2333528 (**1b**), 2333529 (**5**), 2333530 (**7**), 2333531 (**6**) and 2333532 (**8**). For crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d4dt00756e>

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square-planar palladium environment is capable of further reaction. Earlier results by this laboratory also put forward that the said complexes react with small bite strong chelating diphosphines to give species with an uncoordinated phosphorus donor atom,³⁷ thus performing as metalloligands, which were able to coordinate to a second metal atom, providing homo- and hetero-bimetallics. We then sought out to look for analogous systems that would retain the excellent pincer properties of the terdentate [C,N,S] ligands and for this purpose Schiff bases derived from 2-thiomethylaniline were chosen; this changes the thiosemicarbazone sequence $-C(Me)=N-N(H)-C(NHR)-S$ to the corresponding Schiff base one $-C(H)=N-C=C-SMe$. We reasoned that these related systems bearing analogous backbones of nitrogen and sulfur donors would behave likewise and even in the absence of the thiolate sulfur the non-thiolate thiomethyl group would bind well in agreement with Pearson's concept.³⁸ The preparation of [C,N,S] metallacycles can be achieved by quite numerous routes such as reactions with lithium derivatives,³⁹ oxidative addition and photooxidation,⁴⁰ and direct orthometallation for which $Pd(DMSO)_2Cl_2$,⁴¹ $Pd(OAc)_2$, $Li_2[PdCl_4]$ or $Na_2[PdCl_4]$ are amongst the more common reagents. The lithium salt has proven to be a quite useful palladium source for the synthesis of palladacycles, and was used in the present preparations, albeit requires prior synthesis of the salt using moisture-sensitive reagents; therefore, the commercially available sodium salt was also used to compare results and to reduce the synthetic steps. Thus, the latter two were chosen and although the initial steps seemed to agree with the expectations the ensuing iminic metalloligands and the corresponding bimetallics similar to those mentioned above, could not be prepared from the sodium salt, drifting the process to a different route: we tentatively attribute this to partial hydrolysis of the iminic ligand. The spontaneous decay of the products yielded unprecedented rearrangements producing tri- and tetranuclear homometallic complexes, with the methylthioaniline precursor simultaneously acting as a chelating and bridging ligand, leading to new insights into their chemistry. This led us to study the reactivity of the 2-thiomethylaniline itself to test our hypothesis. Furthermore, the bimetallic palladium/tungsten also decayed on recrystallization to yield a pentanuclear heterometallic complex. A more recent example related to spontaneous palladacycle disruption has been reported by us related to the Schiff base palladacycles: an innovate structural rearrangement from single-nuclear to double-nuclear pseudo-penta-coordinated complexes, that we dare say is even more surprising since it could be termed as a special case of self-cyclopalladation.⁴² We tentatively coin these processes as typical cases of serendipity in palladacycle chemistry, which on the other hand put forward novel and exciting reactivity patterns yet to be accounted for, developing new substances that may be of use in any of the fields of application of these compounds.

In this work we report palladacycles bearing tridentate [C,N,S] Schiff base ligands and differing palladium salts, together with the corresponding reactions with mono- and

diphosphines, leading to the discovery of new multinuclear complexes.

Experimental section

General procedures

Solvents were purified by standard methods. Chemicals (lithium chloride, palladium(II) chloride), the phosphines PPh_3 and $Ph_2PCH_2PPh_2$ (dppm), aldehydes and 2-thiomethyl aniline were used as supplied from commercial sources. Lithium tetrachloropalladate was made *in situ* by treating palladium(II) chloride with lithium chloride in methanol. $Ph_2PCH_2P(Ph_2)W(CO)_5$ was prepared by literature synthesis. Microanalyses were carried out at the Servicio de Análisis Elemental at the University of Santiago using a FISONs elemental analyzer, Model 1108. IR spectra were recorded as KBr pellets or polythene discs on BRUKER Model IFS-66v and IR-FT Mattson Model Cygnus-100 spectrophotometers, and on a JASCO FT/IR-4600 spectrometer equipped with an ATR, model ATR-PRO ONE. NMR spectra were obtained as $CDCl_3$, $DMSO-d_6$ or Me_2CO-d_6 solutions as appropriate and referenced to $SiMe_4$ (1H) or 85% H_3PO_4 ($^{31}P-\{^1H\}$) and were recorded on BRUKER DPX 250 and Varian Inova 400 spectrometers. All chemical shifts, in ppm, were reported downfield from the standards.

Syntheses

Preparation of the ligands

The corresponding aldehyde and 2-thiomethyl aniline were added together in chloroform (*ca.* 30 cm³) in a round-bottomed flask to give a pale-yellow solution which was refluxed in a modified Dean-Stark apparatus under dry nitrogen for 24 h, after which the resulting yellow to dark-yellow solution was cooled to room temperature and the solvent removed under reduced pressure.

3,4-(OMe)₂C₆H₃C(H)=N[2-(SMe)C₆H₄] **a**. Yellow solid. Yield: 87%. 1H NMR (400 MHz, $DMSO-d_6$) δ 8.40 (s, 1H, HC=N), 7.66 (s, 1H, H2), 7.47 (dd, $^3J = 8.3$ Hz, $^4J = 1.9$ Hz, 1H, H6), 7.24 (td, $^3J = 7.3$ Hz, $^4J = 1.7$ Hz, 1H, H10), 7.19 (d, $^3J = 7.3$ Hz, 1H, H11), 7.15 (td, $^3J = 7.3$ Hz, $^4J = 1.7$ Hz, 1H, H9), 7.08 (dd, $^3J = 8.3$ Hz, $^4J = 2.0$ Hz, 1H, H5), 7.04 (dd, $^3J = 7.6$ Hz, $^4J = 1.7$ Hz, 1H, H8), 3.89 (s, 6H, OMe), 2.42 (s, 3H, SMe). IR cm^{-1} $\nu(C=N)$ 1618. Anal. found: C, 67.1; H, 5.9; N, 5.0; S, 10.9%, $C_{16}H_{17}NO_2S$ (287.38 g mol⁻¹) requires C, 66.9; H, 6.0; N, 4.9; S, 11.2%.

3-Me-4-OMeC₆H₃C(H)=N[2-(SMe)C₆H₄] **b**. Yellow solid. Yield: 92%. 1H NMR (400 MHz, $DMSO-d_6$) δ 8.39 (s, 1H, HC=N), 7.82 (d, $^4J = 2.1$ Hz, 1H, H2), 7.77 (dd, $^3J = 8.4$ Hz, $^4J = 2.3$ Hz, 1H, H6), 7.23 (td, $^3J = 7.4$ Hz, $^4J = 1.7$ Hz, 1H, H10), 7.18 (dd, $^3J = 7.7$ Hz, $^4J = 1.7$ Hz, 1H, H11), 7.15 (td, $^3J = 7.4$ Hz, $^4J = 1.8$ Hz, 1H), 7.06 (d, $^3J = 8.4$ Hz, 1H, H5), 7.03 (dd, $^3J = 7.5$ Hz, $^4J = 1.6$ Hz, 1H, H8), 3.93 (s, 3H, OMe), 2.42 (s, 3H, SMe), 2.25 (s, 3H, Me). IR cm^{-1} $\nu(C=N)$ 1625. Anal. found: C, 70.5; H, 6.2; N, 5.2; S, 11.9%, $C_{16}H_{17}NOS$ (271.38 g mol⁻¹) requires C, 70.8; H, 6.3; N, 5.2; S, 11.8%.



3,4-(OCH₂CH₂O)C₆H₃C(H)=N[2-(SMe)C₆H₄] **c**. Orange oil. Yield: 88%. ¹H NMR (400 MHz, acetone-*d*₆) δ 8.38 (s, 1H, HC=N), 7.52 (s, 1H, H2), 7.46 (d, ³J = 8.7 Hz, 1H, H6), 7.23 (m, 2H, H9/H11), 7.18–7.13 (m, 1H), 7.04 (d, ³J = 8.2 Hz, 1H, H8), 6.96 (d, ³J = 8.3 Hz, 1H, H5), 4.34 (d, ³J = 5.4 Hz, 4H, CH₂), 2.42 (s, 3H, SMe). IR cm⁻¹ ν(C=N) 1621. Anal. found: C, 67.1; H, 5.3; N, 4.7; S, 11.5%, C₁₆H₁₅NO₂S (285.36 g mol⁻¹) requires C, 67.3; H, 5.3; N, 4.9; S, 11.2%.

4-OMeC₆H₄C(H)=N[2-(SMe)C₆H₄] **d**. Yellow oil. Yield 85%. ¹H NMR (250 MHz, DMSO-*d*₆) δ 8.44 (s, 1H, HC=N), 7.88 (vd, *N* = 8.0 Hz, 2H, H2, H6), 7.10–7.30 (m, 4H, H9, H10, H11, H12), 7.07 (vd, *N* = 8.0 Hz, 2H, H3, H5), 3.82 (s, 3H, OMe), 2.37 (s, 3H, SMe). IR cm⁻¹ ν(C=N) 1626. Anal. found: C, 70.1; H, 6.0; N, 5.7; S, 12.3%, C₁₅H₁₅NOS (257.35 g mol⁻¹) requires C, 70.0; H, 5.9; N, 5.4; S, 12.5%.

2,4-(OMe)₂C₆H₄C(H)=N[2-(SMe)C₆H₄] **e**. Yellow oil. Yield 82%. ¹H NMR (250 MHz, CDCl₃) δ 8.73 (s, 1H, HC=N), 8.19 (d, ³J(H6H5) = 8.7 Hz, 1H, H6), 6.93–7.17 (m, 4H, H9, H10, H11, H12), 6.56 (dd, ³J(H5H6) = 8.7 Hz, ⁴J(H5H3) = 2.3 Hz, 1H, H5), 6.43 (d, ⁴J(H3H5) = 2.3 Hz, 1H, H3), 3.84 (s, 3H, OMe), 3.82 (s, 3H, OMe), 2.42 (s, 3H, SMe). IR cm⁻¹ ν(C=N) 1601. Anal. found: C, 67.0; H, 5.9; N, 5.0; S, 11.0%, C₁₆H₁₇NO₂S (287.38 g mol⁻¹) requires C, 66.8; H, 6.0; N, 4.9; S, 11.2%.

2,3,4-(OMe)₃C₆H₄C(H)=N[2-(SMe)C₆H₄] **f**. Yellow oil. Yield 98%. ¹H NMR (250 MHz, CDCl₃): δ 8.65 (s, 1H, HC=N), 7.97 (d, ³J(H6H5) = 8.8 Hz, 1H, H6), 6.70–7.18 (m, 4H, H9, H10, H11, H12), 6.96 (d, ³J(H5H6) = 8.8 Hz, 1H, H5), 3.94 (s, 3H, OMe), 3.90 (s, 3H, OMe), 3.87 (s, 3H, OMe), 2.43 (s, 3H, SMe). IR cm⁻¹ ν(C=N) 1623. Anal. found: C, 64.1; H, 6.0; N, 4.5; S, 10.2%, C₁₇H₁₉NO₃S (317.40 g mol⁻¹) requires C, 64.3; H, 6.0; N, 4.4; S, 10.1%.

Preparation of the chloride compounds

Route a: Palladium chloride and lithium chloride were added together in oxygen-free methanol in a carousel flask under argon. The mixture was stirred at room temperature until a reddish color appeared. Then, the ligand was added and a color change was observed, followed by turbidity and by the formation of a solid within the solution. The reaction mixture was heated to 70 °C for 4 h and one equivalent of sodium acetate was added, which produced the instantaneous formation of an orange solid that was separated by centrifugation.

Route b: In a 100 mL round bottom flask the ligand was dissolved in methanol with stirring and at room temperature. Then, sodium tetrachloropalladate was added, followed by sodium acetate, and upon further stirring the formation of an orange precipitate was observed. The solid was separated by filtration, washed and dried under vacuum.

Route c (for 1d, 1e, 1f): To a stirred dark-red solution of lithium tetrachloropalladate(n) in methanol the ligand, **d**, **e**, **f**, was added and the mixture was refluxed for 1 h under dry dinitrogen. After cooling to room temperature sodium acetate was added to the resulting solution. The solid formed was filtered off, washed with ethanol and air-dried.

[Pd{3,4-(OMe)₂C₆H₄C(H)=N[2-(SMe)C₆H₄]}(Cl)] **1a**. Orange solid. Yield: 58%. ¹H NMR (400 MHz, CDCl₃) δ 8.51 (s, 1H, HC=N), 7.60 (d, ³J = 8.0 Hz, 1H, H11), 7.57 (t, ³J = 8.0 Hz, 1H, H10), 7.46 (s, 1H, H2), 7.45 (td, ³J = 8.4 Hz, ⁴J = 1.4 Hz, 1H, H9), 7.40–7.33 (m, 1H), 7.02 (s, 1H, H5), 4.01 (s, 3H, OMe), 3.86 (s, 3H, OMe), 2.81 (s, 3H, SMe). IR cm⁻¹ ν(C=N) 1579; ν(Pd–Cl) 322. Anal. found: C, 45.1; H, 3.8; N, 3.5; S, 7.3%, C₁₆H₁₆ClNO₂PdS (428.24 g mol⁻¹) requires C, 44.9; H, 3.8; N, 3.3; S, 7.5%.

[Pd{3-Me-4-OMeC₆H₄C(H)=N[2-(SMe)C₆H₄]}(Cl)] **1b**. Orange solid. Yield: 63%. ¹H NMR (400 MHz, CDCl₃) δ 8.47 (s, 1H, HC=N), 7.60 (dd, ³J = 8.5 Hz, ⁴J = 1.2 Hz, 1H), 7.57 (dd, ³J = 7.8 Hz, ⁴J = 1.5 Hz, 1H), 7.44 (td, ³J = 8.4 Hz, ⁴J = 1.5 Hz, 1H), 7.39 (s, 1H, H2), 7.38–7.29 (m, 2H), 3.96 (s, 3H, OMe), 2.81 (s, 3H, SMe), 2.14 (s, 3H, Me). IR cm⁻¹ ν(C=N) 1581; ν(Pd–Cl) 329. Anal. found: C, 46.7; H, 3.9; N, 3.6; S, 7.9%, C₁₆H₁₆ClNOPdS (412.24 g mol⁻¹) requires C, 46.6; H, 3.9; N, 3.4; S, 7.8%.

[Pd{3,4-(OCH₂CH₂O)C₆H₄C(H)=N[2-(SMe)C₆H₄]}(Cl)] **1c**. Orange solid. Yield: 74%. ¹H NMR (400 MHz, acetone-*d*₆) δ 9.01 (s, 1H, HC=N), 7.99 (d, ³J = 8.4 Hz, 1H, H11), 7.81 (d, ³J = 7.8 Hz, 1H, H8), 7.58 (t, ³J = 7.4 Hz, 3H, H10), 7.48 (t, ³J = 8.0 Hz, 1H, H9), 7.21 (s, 1H, H2), 7.14 (s, 1H, H5), 7.34 (d, *J* = 4.1 Hz, 2H, CH₂), 4.27 (s, 2H, CH₂), 2.82 (d, *J* = 1.6 Hz, 3H, SMe). IR cm⁻¹ ν(C=N) 1581; ν(Pd–Cl) 327. Anal. found: C, 44.8; H, 3.2; N, 3.1; S, 7.2%, C₁₆H₁₄ClNO₂PdS (426.22 g mol⁻¹) requires C, 45.1; H, 3.3; N, 3.3; S, 7.5%.

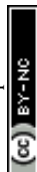
[Pd{4-OMeC₆H₃C(H)=N[2-(SMe)C₆H₄]}(Cl)] **1d**. Yellow solid. Yield 83%. ¹H NMR (250 MHz, DMSO-*d*₆): δ 9.12 (s, 1H, HC=N), 7.98 (d, ³J(H11H12) = 8.4 Hz, 1H, H12), 7.83 (d, ³J(H9H10) = 7.9 Hz, 1H, H9), 7.55 (t, ³J(H10H11) = 8.0 Hz, 1H, H10), 7.53 (d, ³J(H2H3) = 8.8 Hz, 1H, H2), 7.44 (t, 1H, H11), 7.11 (d, ⁴J(H5H3) = 2.7 Hz, 1H, H5), 6.71 (dd, 1H, H3), 3.80 (s, 3H, OCH₃), 2.75 (s, 3H, SCH₃). IR 1603 ν(C=N), 315 ν(Pd–Cl_{trans-N}) cm⁻¹. Anal. found: C, 45.0; H, 3.4; N, 3.4; S, 8.0%, C₁₅H₁₄ClNOPdS (398.22 g mol⁻¹) requires C, 45.2; H, 3.5; N, 3.5; S, 8.1%.

[Pd{2,4-(OMe)₂C₆H₄C(H)=N[2-(SMe)C₆H₄]}(Cl)] **1e**. Orange solid. Yield 77%. ¹H NMR (250 MHz, CDCl₃) δ 8.77 (s, 1H, HC=N), 7.61 (d, ³J(H11H12) = 8.2 Hz, 1H, H12), 7.51 (d, ³J(H9H10) = 7.8 Hz, 1H, H9), 7.39 (t, 1H, H10), 7.27 (t, 1H, H11), 7.03 (d, ⁴J(H5H3) = 2.1 Hz, 1H, H5), 6.06 (d, ⁴J(H3H5) = 2.1 Hz, 1H, H3), 3.89 (s, 3H, OMe), 3.80 (s, 3H, OMe), 2.77 (s, 3H, SMe). IR 1585 ν(C=N), 332 ν(Pd–Cl_{trans-N}) cm⁻¹. Anal. found: C, 45.1; H, 3.8; N, 3.2; S, 7.4%, C₁₆H₁₆ClNO₂PdS (428.24 g mol⁻¹) requires C, 44.9; H, 3.8; N, 3.3; S, 7.5%.

[Pd{2,3,4-(OMe)₃C₆H₄C(H)=N[2-(SMe)C₆H₄]}(Cl)] **1f**. Yellow solid. Yield 82%. ¹H NMR (250 MHz, CDCl₃) δ 8.73 (s, 1H, HC=N), 7.64 (d, ³J(H12H11) = 8.3 Hz, 1H, H12), 7.54 (d, ³J(H9H10) = 7.7 Hz, 1H, H9), 7.42 (t, ³J(H10H11) = 7.2 Hz, 1H, H10), 7.15 (s, 1H, H5); 7.30 (t, 1H, H11), 4.02 (s, 3H, OMe), 3.95 (s, 3H, OMe), 3.77 (s, 3H, OMe), 2.76 (s, 3H, SMe). IR 1606 ν(C=N), 333 ν(Pd–Cl_{trans-N}) cm⁻¹. Anal. found: C, 44.5; H, 3.9; N, 3.2; S, 7.1%, C₁₇H₁₈ClNO₃PdS (458.27 g mol⁻¹) requires C, 44.6; H, 4.0; N, 3.1; S, 7.0%.

Preparation of the triphenylphosphine palladacycles

The appropriate palladacycle and silver perchlorate were added in acetone (15 mL) in a carousel tube to give a light orange



solution, which was stirred for 10 min. Then, the solution becomes dark orange and the resulting white solid (AgCl) was removed by centrifugation prior to addition of triphenylphosphine. Removal of the solvent under reduced pressure gave the expected complex as an orange solid, which was filtered off and dried.

[Pd{3,4-(OMe)₂C₆H₂C(H)=N[2-(SMe)C₆H₄]}(PPh₃)](ClO₄) 2a. Orange solid. Yield: 78%. ¹H NMR (400 MHz, acetone-*d*₆) δ 9.29 (d, ⁴*J*_{P-H} = 9.3 Hz, 1H, HC=N), 8.05 (d, ³*J* = 8.4 Hz, 1H, H11), 7.89–7.81 (m, 7H), 7.74–7.51 (m, 9H), 7.43 (s, 1H, H2), 6.83 (t, ³*J* = 7.8 Hz, 1H, H9), 6.61 (t, ³*J* = 7.8 Hz, 1H, H10), 6.05 (d, ⁴*J*_{P-H} = 5.3 Hz, 1H, H5), 3.76 (s, 3H, OMe), 2.93 (s, 3H, OMe), 2.12 (s, 3H, SMe). ³¹P-NMR (400 MHz, acetone-*d*₆) δ 38.89. IR ν(C=N) 1582; ν(ClO₄) 1094 cm⁻¹. Anal. found: C, 53.8; H, 3.9; N, 1.8; S, 4.1%, C₃₄H₃₁ClNO₆PPdS (754.53 g mol⁻¹) requires C, 54.1; H, 4.1; N, 1.9; S, 4.3%.

[Pd{3-Me-4-OMeC₆H₂C(H)=N[2-(SMe)C₆H₄]}(PPh₃)](ClO₄) 2b. Orange solid. Yield: 80%. ¹H NMR (400 MHz, acetone-*d*₆) δ 9.25 (d, ⁴*J*_{P-H} = 9.1 Hz, 1H, HC=N), 8.06 (d, ³*J* = 8.6 Hz, 1H, H11), 7.85 (dd, *J* = 12.4, 8.0 Hz, 6H), 7.74–7.56 (m, 9H), 7.51 (d, *J* = 6.8 Hz, 11H), 7.43 (s, 1H, H2), 6.84 (t, *J* = 7.9 Hz, 1H, H9), 6.62 (t, *J* = 7.9 Hz, 1H, H10), 6.05 (d, ⁴*J*_{P-H} = 4.3 Hz, 1H, H5), 2.95 (s, 3H, OMe), 2.26 (s, 3H, Me), 2.12 (s, 3H, SMe). ³¹P-NMR (400 MHz, acetone-*d*₆) δ 37.49. IR cm⁻¹ ν(C=N) 1582; ν(ClO₄) 1091. Anal. found: C, 55.1; H, 4.1; N, 1.9; S, 4.4%, C₃₄H₃₁ClNO₅PPdS (738.53 g mol⁻¹) requires C, 55.3; H, 4.2; N, 1.9; S, 4.3%.

[Pd{3,4-(OCH₂CH₂O)C₆H₂C(H)=N[2-(SMe)C₆H₄]}(PPh₃)](ClO₄) 2c. Orange solid. Yield: 85%. ¹H NMR (400 MHz, acetone-*d*₆) δ 9.30 (d, ⁴*J*_{P-H} = 9.0 Hz, 1H, HC=N), 8.10 (d, ³*J* = 8.3 Hz, 1H, H11), 8.06–7.97 (m, 6H), 7.78–7.49 (m, 9H), 7.46 (t, ³*J* = 7.6 Hz, 1H, H10), 7.36 (m, 1H, H9), 7.09 (s, 1H, H2), 7.02 (s, 1H, H2), 5.95 (d, ⁴*J*_{P-H} = 5.0 Hz, 1H, H5), 4.17–4.10 (m, 4H, OCH₂CH₂O), 2.14 (s, 3H, SMe). ³¹P-NMR (400 MHz, acetone-*d*₆) δ 38.54. IR cm⁻¹ ν(C=N) 1576; ν(ClO₄) 1094. Anal. found: C, 54.5; H, 3.9; N, 2.1; S, 4.1%, C₃₄H₂₉ClNO₆PPdS (752.51 g mol⁻¹) requires C, 54.3; H, 3.9; N, 1.9; S, 4.3%.

Reactivity of 2-methylthio aniline

Route a: Palladium acetate was introduced into a carousel tube fitted with a stirring bar. 10 mL of toluene are added, and a partial dissolution of palladium salt is observed. Methylthioaniline is then introduced, and it is observed that the solution becomes orange. It is allowed to react with stirring at 50 °C for 24 h, after which the formation of a yellow solid is observed within the solution that is separated by centrifugation. The supernatant is brought to dryness, resulting in an orange solid. ¹H NMR (400 MHz, acetone-*d*₆) δ 7.27 (d, ³*J* = 7.6 Hz, 1H), 7.02 (t, ³*J* = 7.7 Hz, 1H), 6.77 (d, ³*J* = 8.1 Hz, 1H), 6.59 (t, ³*J* = 7.5 Hz, 1H), 4.91 (d, ³*J* = 10.2 Hz, 2H), 2.31 (s, 3H).

Route b: In a carousel tube fitted with a stirring bar sodium tetrachloropalladate was added in methanol (10 mL) and a reddish solution was formed; which quickly changes to yellow upon addition of methylthioaniline. The reaction mixture was stirred for 24 h and a white solid formed was separated by centrifugation, after which the resulting solution was reduced to

low volume to give an orange solid. ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.84 (d, ³*J* = 7.7 Hz, 1H), 7.48 (t, ³*J* = 7.5 Hz, 1H), 7.42 (t, ³*J* = 7.5 Hz, 1H), 7.33 (d, ³*J* = 7.9 Hz, 1H), 7.18 (d, ³*J* = 7.7 Hz, 1H), 6.97 (t, ³*J* = 7.7 Hz, 1H), 6.68 (d, ³*J* = 8.0 Hz, 1H), 6.53 (t, ³*J* = 7.5 Hz, 1H), 5.16 (s, 2H, NH), 2.84 (s, 3H, SMe), 2.29 (s, 3H, SMe).

Preparation of the diphosphine palladacycles

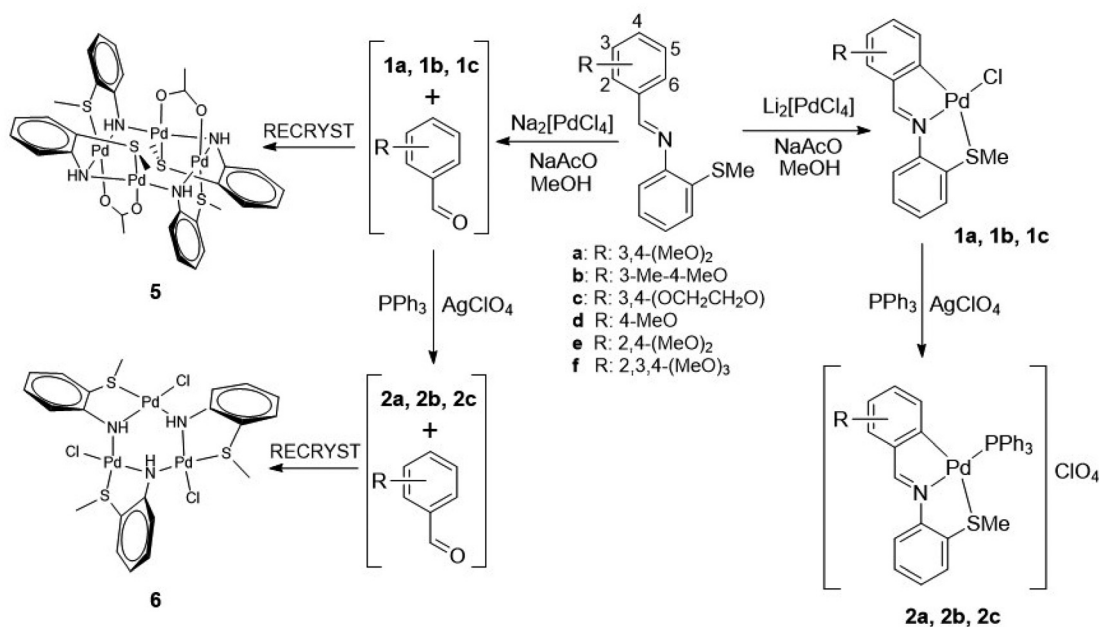
[Pd{4-OMeC₆H₃C(H)=N[2-(SMe)C₆H₄]}(PPh₂CH₂PPh₂-P)](ClO₄) (3d). Silver perchlorate (10.4 mg, 0.05 mmol) was added to a suspension of the cyclometallated complex **1a** (20 mg, 0.05 mmol) in acetone (15 cm³). The mixture was stirred for 4 h at r.t. and filtered over Celite to remove the silver chloride precipitate. PPh₂CH₂PPh₂ (19 mg, 0.05 mmol) was added to the filtrate and the solution stirred for 24 h at r.t., the solvent was removed and the residue was recrystallized from dichloromethane/hexane. Orange solid. Yield 78%. ¹H NMR (400 MHz, CDCl₃) δ 8.88 (d, 1H, HC=N, ⁴*J*_{P-H} = 8.4 Hz), 7.30–7.80 (m, 20H, PPh₂); H₂, 7.70–7.00 (H10–H12 hidden by the resonance of aromatic phosphine system), 7.15 (d, 1H, H9), 6.61 (d, 1H, H3, ³*J*(H2H3) = 7.5 Hz), 5.84 (s, 1H, H5), 4.19 (ta, 2H, PCH₂P, ²*J*(HP) = 2.4 Hz), 3.22 (s, 3H, OCH₃), 2.07 (s, 3H, SCH₃). ³¹P NMR (400 MHz, CDCl₃) δ -23.60 (d, ²*J*(PP) = 51.5 Hz); 31.30 (d, ²*J*(PP) = 51.5 Hz). IR cm⁻¹ ν(C=N) 1598; ν(ClO₄) 1093. Anal. found: C, 56.8; H, 4.3; N, 1.7; S, 4.3%, C₄₀H₃₆ClNO₅P₂PdS (846.60 g mol⁻¹) requires C, 57.0; H, 4.2; N, 1.6; S, 3.8%.

[Pd{2,4-(OMe)₂C₆H₃C(H)=N[2-(SMe)C₆H₄]}(PPh₂CH₂P(Ph₂W(CO)₅-P)](ClO₄) (4d). To a suspension of **1e** (20 mg, 0.05 mmol) in acetone (15 cm³). AgClO₄ was added. The mixture was stirred for 4 h, after which time the silver chloride formed was filtered off through Celite. PPh₂CH₂P(Ph₂W(CO)₅) (11 mg, 0.025 mmol) was added to the filtrate and the solution stirred for 4 h; reducing to low volume gave a solid which was filtered off and dried. Yellow solid. Yield 53% (1200.52). Calc. found. ¹H NMR (400 MHz, CDCl₃) δ 8.90 (d, 1H, HC=N, ⁴*J*_{P-H} = 7.6 Hz), 7.70–7.00 (H9–H12 hidden by the resonance of aromatic phosphine system), 6.42 (d, ²*J*(PP) = 72.0 Hz, ¹*J*(PW) = 247.9 Hz), 6.02 (d, 1H, H3, ⁴*J*(H3H5) = 3.2 Hz), 5.55 (dd, 1H, H5, ⁴*J*(H5H3) = 3.2 Hz, ⁴*J*(H5P) = 7.1 Hz), 4.93 (t, 1H, CH₂, ²*J*(HP) = 9.3 Hz, ²*J*(HP) = 11.5 Hz), 3.98 (dd, 1H, CH₂, ²*J*(HP) = 6.3 Hz, ²*J*(HP) = 11.7 Hz), 3.82 (s, 3H, OCH₃), 3.40 (s, 3H, OCH₃), 1.70 (s, 3H, SCH₃). ³¹P NMR (400 MHz, CDCl₃) δ 26.6 (d, ²*J*(PP) = 72.0 Hz); IR cm⁻¹ ν(C=N) 1583; ν(ClO₄) 1095. Anal. found: C, 45.8; H, 3.3; N, 1.7; S, 3.2%, C₄₆H₃₈ClNO₁₁P₂PdSW (1200.52 g mol⁻¹) requires C, 46.0; H, 3.2; N, 1.2; S, 2.7%.

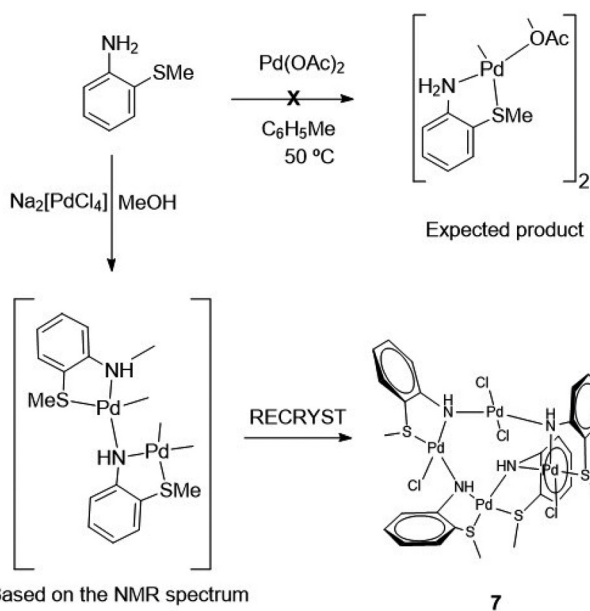
Results and discussion

For the convenience of the reader the compounds and reactions are shown in Schemes 1–3. The compounds described in this paper were characterized by elemental analysis (C, H, N, S), and by IR spectroscopy, and by ¹H, ³¹P-¹H} spectroscopy and, in part, crystal structure analysis (see Experimental, Table 1 and Fig. 1–5).





Scheme 1 Reaction sequence leading to the synthesis of the compounds.



Scheme 2 Reactivity of 2-thiomethyl aniline with differing palladium reagents.

The Schiff base ligands **a–f** were prepared by reaction of 2-thiomethylaniline with the corresponding aldehyde to give pure air-stable solids which were fully characterized. Distinctive of the spectrum of **d** were the two virtual doublets stemming from the aromatic AA'XX' spin system with $N = 8.0$ ppm. Treatment of the ligands with $\text{Li}_2[\text{PdCl}_4]/\text{NaAcO}$ in methanol gave the palladacycles **1a–1c** (Scheme 1) and **1d–1f** (Scheme 3) that were isolated as air-stable solids with the

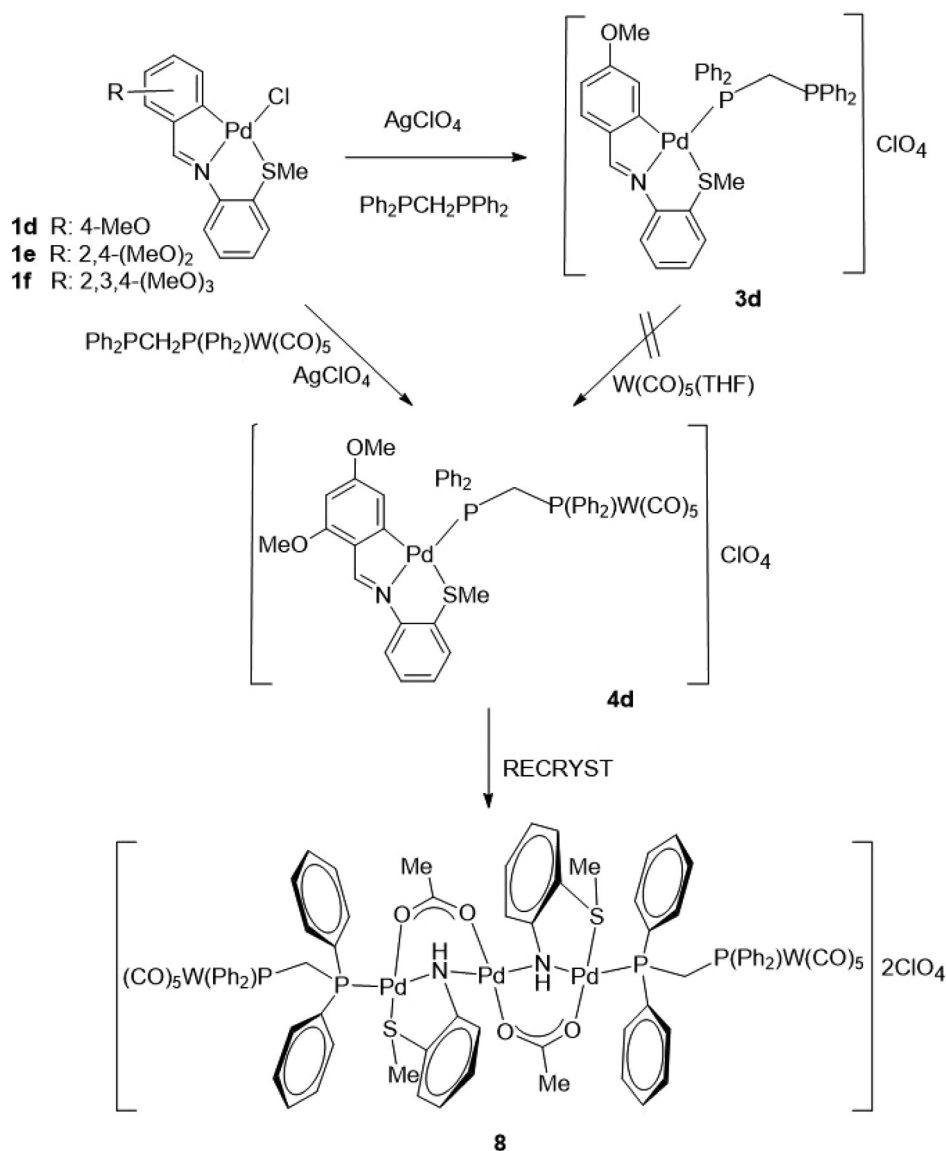
ligand in a tridentate [C,N,S] coordination mode; preparative details and characteristic microanalytical and spectroscopic data are given in the Experimental section. Noteworthy to mention are the shift of the $\nu(\text{C}=\text{N})$ stretch to lower wavenumbers by *ca.* 40 cm^{-1} in the IR spectra, and absence of the C(6)–H resonance in the NMR spectra;⁴³ also, the SMe resonance was downfield shifted in the ¹H NMR spectra, *ca.* 0.4 ppm, in agreement with Pd–S coordination, and the metallated ligand of **1d** showed the absence of the AA'XX' system consequent on Pd–C bond formation.

Crystal structure of **1b**

Suitable crystals were grown by slow evaporation of a chloroform solution. The crystal structure of **1b** (Fig. 1 and Table 1) consists of molecules with the palladium(II) atom bonded in a slightly distorted square-planar environment to four different donor atoms, the aryl C(6) carbon, the iminic N(1) nitrogen, and the S(1) sulfur atoms, of the tridentate iminic and to the chlorine atom Cl(1). The sulfur atom in SMe becomes a chiral center upon metalation, and in the structure there is a racemic mixture of both enantiomers. The angles between adjacent atoms in the palladium coordination sphere are *ca.* 90° with the most noticeable distortion in the N(1)Pd(1)C(6) angle of $81.7(2)^\circ$, a consequence of chelation; the sum of angles around the palladium atom is 360.03° . All bond lengths are within the expected range, with allowance for Pd(1)C(1) length, of $2.044(4)\text{ \AA}$, shorter than the expected value of 2.081 \AA ⁴⁴ suggesting some degree of multiple bond character in the PdC(aryl) linkage.⁴⁵

Reaction of **1a–1c** with $\text{PPh}_3/\text{AgClO}_4$ gave complexes **2a–2c**, after abstraction of the chloride ion as AgCl, which were fully characterized (see Experimental). Attempts to produce species





Scheme 3 Reaction sequence leading to the compounds with diphosphine.

with simultaneous linkage of the phosphine and chloride ligands to the metal were to no avail; this is in keeping with a rather strong Pd–S bond. The IR spectra showed absence and of the $\nu(\text{Pd}-\text{Cl})$ band; whilst the ^1H NMR spectra the H(5) was upfield shifted and coupled to the phosphorus resonance.

To study the suitability of other metallating agents a slightly different synthetic approach was tested with ligands **a-c**; this allowed disclosure of a new performance of the ligands and complexes. Thus, treatment of ligands **a-c** with $\text{Na}_2[\text{PdCl}_4]/\text{NaAcO}$ in methanol gave a solution containing the **1a-1c** complexes, with analogous spectroscopic features as those described above, plus the starting aldehyde and amine, for which the ^1H NMR spectra showed the signals for the $\text{HC}=\text{O}$, NH_2 and SMe resonances *ca.* 10, 6.7 and 2.3 ppm, respectively, together with other aromatic resonances (mixtures type A). This did not seem to be unusual because in the pre-

vious reactions using $\text{Li}_2[\text{PdCl}_4]$ as metal salt, prior to addition of the base, aliquots of the reaction mixture were taken and some free aldehyde was observed due to partial hydrolysis; however, in those cases after addition of NaAcO and ensuing work up the final compounds were obtained pure (*vide supra*). Then, treatment of the said mixture A with $\text{PPh}_3/\text{AgClO}_4$ yielded compounds **2a-2c** impurified with free aldehyde and amine (mixtures type B). To separate the palladacycles and confirm the alternative use of the sodium salt as a metallating agent, recrystallization was performed for both types of mixtures.

Crystal structure of 5

Suitable crystals of mixture A were grown from a chloroform solution, labelled 5. The crystal structure of 5 (Fig. 2 and Table 1) consists of molecules with the palladium(II) atom



Table 1 Crystallographic data for 1b, 5–8

Compound	1b	5	6	7	8
Empirical formula	C ₁₆ H ₁₆ ClNOPdS	C ₁₇ H ₂₀ Cl ₄ N ₂ O ₆ Pd ₂ S ₂	C ₂₅ H ₃₆ Cl ₃ N ₃ O ₂ Pd ₃ S ₅	C ₃₁ H ₃₅ Cl ₁₃ N ₄ Pd ₄ S ₄	C ₇₈ H ₆₆ Cl ₂ N ₂ O ₂₂ Pd ₃ S ₂ W ₂
Formula weight	412.245	767.131	996.518	1479.647	2329.12
Temperature/K	100.0	100.0	100.0	100.00	100.0
Crystal system	Monoclinic	Triclinic	Monoclinic	Orthorhombic	Triclinic
Space group	<i>P2₁/c</i>	<i>P1</i>	<i>P2₁/n</i>	<i>Pbca</i>	<i>P1</i>
<i>a</i> /Å	8.1340(2)	11.6987(6)	9.6057(5)	10.6947(8)	10.8665(13)
<i>b</i> /Å	11.6466(3)	15.0875(8)	19.0596(10)	22.0850(16)	12.0797(14)
<i>c</i> /Å	17.0711(4)	18.3377(9)	19.8471(11)	40.285(3)	19.070(2)
α /°	90	105.262(3)	90	90	72.291(7)
β /°	101.9138(10)	104.871(3)	91.4728(17)	90	89.037(7)
γ /°	90	107.653(4)	90	90	78.172(7)
Volume/Å ³	1582.37(7)	2769.0(3)	3632.4(3)	9515.0(12)	2331.2(5)
Z	4	4	4	8	1
$\rho_{\text{calc.}}/\text{g cm}^{-3}$	1.730	1.840	1.822	2.066	1.659
μ/mm^{-1}	1.471	15.748	2.006	2.425	3.262
<i>F</i> (000)	821.5	1518.5	1961.1	5733.3	1136
Crystal size/mm ³	0.156 × 0.127 × 0.092	0.08 × 0.03 × 0.02	0.14 × 0.09 × 0.05	0.09 × 0.07 × 0.03	0.200 × 0.090 × 0.030
Radiation	Mo K α (λ = 0.71073)	Cu K α (λ = 1.54178)	Mo K α (λ = 0.71073)	Mo K α (λ = 0.71073)	Mo K α (λ = 0.71073)
2 θ /°	4.88 to 77.14	6.62 to 140.14	4.74 to 56.76	4.32 to 56.68	1.810 to 26.445
Index ranges	−14 ≤ <i>h</i> ≤ 14, −20 ≤ <i>k</i> ≤ 19, −29 ≤ <i>l</i> ≤ 29	−14 ≤ <i>h</i> ≤ 14, −18 ≤ <i>k</i> ≤ 18, −22 ≤ <i>l</i> ≤ 22	−12 ≤ <i>h</i> ≤ 12, −25 ≤ <i>k</i> ≤ 25, −25 ≤ <i>l</i> ≤ 26	−14 ≤ <i>h</i> ≤ 14, −29 ≤ <i>k</i> ≤ 29, −33 ≤ <i>l</i> ≤ 53	−13 ≤ <i>h</i> ≤ 13, −15 ≤ <i>k</i> ≤ 15, −23 ≤ <i>l</i> ≤ 23
Reflections collected	63 757	68 334	86 053	98 993	70 681
Independent reflections	8909 [<i>R</i> _{int} = 0.0353, <i>R</i> _{sigma} = 0.0233]	10 523 [<i>R</i> _{int} = 0.1983, <i>R</i> _{sigma} = 0.1049]	9079 [<i>R</i> _{int} = 0.0378, <i>R</i> _{sigma} = 0.0198]	11 826 [<i>R</i> _{int} = 0.0686, <i>R</i> _{sigma} = 0.0392]	9506 [<i>R</i> _{int} = 0.1012]
Data/restraints/parameters	8909/0/193	10 523/0/602	9079/24/459	11 826/24/574	9506/439/550
Goodness-of-fit on <i>F</i> ²	1.037	1.020	1.050	1.045	1.087
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0232, <i>wR</i> ₂ = 0.0510	<i>R</i> ₁ = 0.0676, <i>wR</i> ₂ = 0.1638	<i>R</i> ₁ = 0.0328, <i>wR</i> ₂ = 0.0737	<i>R</i> ₁ = 0.0727, <i>wR</i> ₂ = 0.1316	<i>R</i> ₁ = 0.0762, <i>wR</i> ₂ = 0.1540
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0312, <i>wR</i> ₂ = 0.0547	<i>R</i> ₁ = 0.1213, <i>wR</i> ₂ = 0.2051	<i>R</i> ₁ = 0.0370, <i>wR</i> ₂ = 0.0764	<i>R</i> ₁ = 0.0832, <i>wR</i> ₂ = 0.1368	<i>R</i> ₁ = 0.1130, <i>wR</i> ₂ = 0.1649
Largest diff. peak/hole/e Å ^{−3}	0.73/−1.16	1.59/−1.82	3.16/−2.83	1.63/−1.91	2.303/−2.307

bonded in a slightly distorted square-planar environment to two mutually perpendicular pairs of [O,O] and [N,S] donors, pertaining to bridging acetate and chelating 2-thiomethylanilide ligands, respectively; the nitrogen atoms in turn act as bridging donors between two palladiums. The nitrogen atoms are arranged in a square-planar geometry and in turn act as bridging donors holding the palladium atoms at a midway distance between each pair of nitrogens to give an eight-membered ring of alternating Pd/N centers. Thus, the palladium coordination planes are set as two pairs of mutually facing parallel planes *ca.* 90° to the Pd₄N₄ ring.

We reasoned that mixture B should produce either crystals of 2a–2c, as appropriate, or a structure analogous to 5 depending on whether or not the acetate ligands were lost in the corresponding preparation. Again, the experimental facts show that an absolutely distinctive structure was obtained: a trinuclear crystal void of any acetate ligands, labelled 6.

Crystal structure of 6

Suitable crystals were grown from mixture B from a DMSO-*d*₆ solution, labelled 6. The crystal structure (Fig. 3 and Table 1) consists of a trinuclear molecule with a central Pd₃N₃ six-membered ring of alternating palladium and nitrogen atoms in a chair conformation, with the Pd(2) and N(10) atoms pointing to opposite directions from the Pd(1)N(8)N(9)Pd(3) plane

(Fig. 5b). Each palladium atom is bonded to a chelating bidentate [N,S] 2-thiomethylanilide, that in turn also coordinates as a bridging ligand between two metal atoms *via* the nitrogen donor. The fourth coordination site at each palladium is occupied by a chloride ligand *trans* to nitrogen for the three metal centers. The palladium coordination planes [S(1)N(8)Cl(1)Pd(1)N(10)] (plane 1), [S(2)N(8)Cl(2)Pd(2)N(9)] (plane 2) and [S(3)N(9)Cl(3)Pd(3)N(10)] (plane 3) are set as follows: 1² 83.44°; 1³ 77.08°; 2³ 79.91°.

In view of this unexpected behavior of the amine ligand stemming from partial hydrolysis of the parent Schiff base, we sought out to study the behavior of free 2-methylthioaniline itself in order to determine if compounds 5 and 6 were produced only from the corresponding palladacycles, or if it was solely dependent on the presence of the free amine. For such a purpose 2-thiomethylaniline was treated independently with Pd(OAc)₂ in toluene or with Na₂[PdCl₄] in methanol (see Scheme 2 and Experimental for preparative details).

The former process gave only the free amine, as was determined by ¹H NMR spectroscopy. However, in the latter case the ¹H NMR spectrum shows there are two singlets assignable to the *SMe* groups and two sets of aromatic peaks containing four doublets and four triplets in agreement with a four-spin system of an *ortho*-substituted phenyl ring. This is a differing situation from that found for compounds 5 and 6, where the



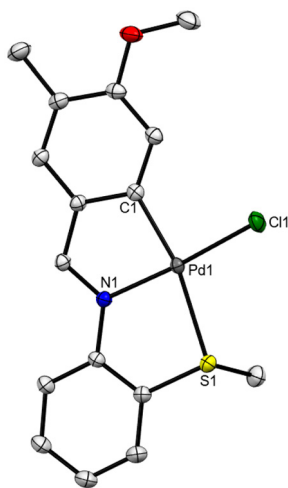


Fig. 1 ORTEP drawing of compound **1b** with thermal ellipsoid plot shown at 50% probability level. Hydrogen atoms and solvent molecules have been omitted for clarity. Selected bond distances (Å) and angles (°): Pd(1)–C(1) 1.9936(11), Pd(1)–N(1) 2.0039(9), Pd(1)–S(1) 2.3987(3), Pd(1)–Cl(1) 2.2963(3), S(1)–Pd(1)–Cl(1) 98.815(10), N(1)–Pd(1)–S(1) 84.63(3), N(1)–Pd(1)–Cl(1) 175.43(3), C(1)–Pd(1)–S(1) 166.53(3), C(1)–Pd(1)–Cl(1) 94.65(3), C(1)–Pd(1)–N(1) 81.91(4).

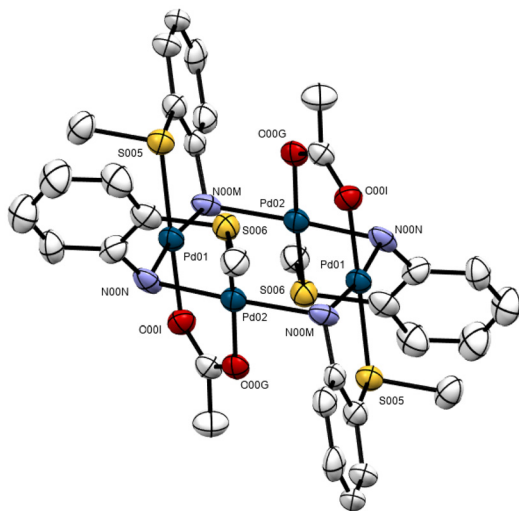


Fig. 2 ORTEP drawing of compound **5** with thermal ellipsoid plot shown at 50% probability level. Hydrogen atoms and solvent molecules have been omitted for clarity. Selected bond distances (Å) and angles (°): Pd(01)–S(005) 2.262(3), Pd(01)–N(00N) 2.065(8), Pd(01)–N(00M) 2.032(9), Pd(01)–O(00I) 2.042(8), N(00N)–Pd(01)–S(005) 99.5(3), N(00N)–Pd(01)–O(00I) 88.1(3), N(00M)–Pd(01)–O(00I) 87.0(3), N(00M)–Pd(01)–S(005) 85.7(3); Pd(02)–O(00G) 2.044(8), Pd(02)–N(00N) 2.014(9), Pd(02)–N(00M) 2.063(9), Pd(02)–S(006) 2.257(3), N(00N)–Pd(02)–S(006) 86.2(3), N(00N)–Pd(02)–O(00G) 91.2(4), N(00M)–Pd(02)–O(00G) 88.4(3), N(00M)–Pd(02)–S(006) 94.4(3).

2-thiomethylanilide ligands were in equivalent chemical environments, pointing to two types of non-equivalent amine molecules that are present in the final compound. Fortunately, single-crystals could be obtained to clarify this finding and the

result is even more fascinating than for structures **5** and **6** (*vide infra*).

Crystal structure of **7**

Suitable crystals were grown from a chloroform solution, labelled **7**. The crystal structure (Fig. 4 and Table 1) consists of four palladium atoms, four chloride and four 2-thiomethylanilide ligands displayed such that there are three types of palladium coordination environments: 2 + 1 + 1. The aniline moieties are linked to the Pd(1), Pd(2) and Pd(4) atoms in a bidentate [N,S] fashion and the four palladium atoms are bonded together *via* the nitrogen from bridging 2-MeC₆H₄NH₂-N units; the chlorine atoms complete the coordination sphere at the metal as terminal ligands. Thus, Pd(1) is bonded to two chelating [N,S] aniline ligands with the donor atoms in a *cis* geometry; Pd(2) and Pd(4) to one chelating amine, a terminal chlorine atom and a nitrogen atom from an adjacent organic ligand; Pd(3) to two mutually *trans* terminal chlorine atoms and two nitrogen donors from nearby amine ligands also in a *trans* arrangement. All of which results in a Pd₄N₄ eight-membered ring of alternating palladium and nitrogen atoms. The palladium coordination planes [Pd(1)N(1)N(4)S(1)S(4)] (1), [Pd(2)N(1)N(2)S(2)Cl(1)] (2), [Pd(3)N(2)N(3)Cl(2)Cl(3)] (3) [Pd(4)N(3)N(4)S(3)Cl(4)] (4) [1² 89.59°; 1³ 87.60°, 1⁴ 86.55°, 2³ 85.92°; 3⁴ 85.81°; 2⁴ 8.99°] are angled *ca.* 90°, save for planes 2 and 4 which are close to a parallel disposition.

Next, we attempted to study the behavior of the **1a–1f** class complexes with diphosphines to determine whether they would give species analogous to the thiosemicarbazone-[C,N,S] palladacycles we have described in the past, *i.e.*, complexes with a mono-coordinated diphosphine and also the ensuing dinuclear compounds with the diphosphine ligand bridging two metal centers; or if alternatively, and given the results depicted above, they would evolve to unprecedented multinuclear compounds; for which purpose we chose compound **1d** and the diphosphine dppm, Ph₂PCH₂PPh₂.

Hence, treatment of **1d** with dppm in 1:1 molar ratio and NaClO₄ gave the hoped for complex **3d** as a pure air-stable solid, which was fully characterized. The ³¹P NMR spectrum displayed two doublets at –23.6 and 31.3 ppm, for the two inequivalent phosphorus nuclei. The resonance at lower frequency was assigned to the non-coordinated phosphorus nucleus; whereas the one at higher frequency was assigned to the phosphorus nucleus bonded to palladium. The HC=N resonance was a doublet coupled to the *trans* phosphorus nucleus (¹J(HiP) = 8.4 Hz). Both the MeO and SMe resonances were shifted to lower frequency *ca.* 0.6 and 0.7 ppm respectively, due to shielding by the phosphine phenyl rings. The proton signal was an apparent triplet from the AA'X'X' four spin system P(CH₂)₂P with an *N* value of 2.4 Hz. Attempts to prepare the heterobimetallic complex **4d** by treatment of **3d** with [W(CO)₅(THF)] gave an untreatable mixture which was not further investigated. Likewise, reaction of **3d** with other substrates bearing labile ligands such as [Fe(CO)₄(THF)] and [Pd(Cl)₂(PhCN)₂], to yield the corresponding dinuclear species were also deemed unsuccessful. Alternatively, reaction of **1d** with [W(CO)₅{Ph₂PCH₂PPh₂-P}] did produce the expected compound **4d**



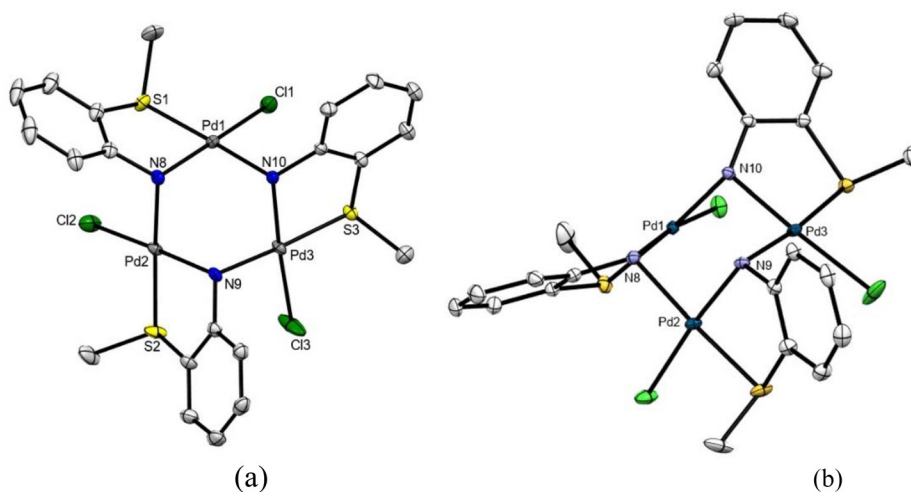


Fig. 3 (a) ORTEP drawing of compound **6** with thermal ellipsoid plot shown at 50% probability level. Hydrogen atoms and solvent molecules have been omitted for clarity. Selected bond distances (Å) and angles (°): Pd(1)–Cl(1) 2.3248(9), Pd(1)–N(8) 2.025(3), Pd(1)–N(10) 2.096(3), Pd(1)–S(1) 2.2803(8), N(10)–Pd(1)–Cl(1) 94.61(8), N(8)–Pd(1)–S(1) 84.21(8), N(8)–Pd(1)–N(10) 90.77(11), Cl(1)–Pd(1)–S(1) 90.72(3); Pd(2)–Cl(2) 2.3286(9), Pd(2)–N(8) 2.079(3), Pd(2)–N(9) 2.026(3), Pd(2)–S(2) 2.2863(9), N(8)–Pd(2)–Cl(2) 95.26(8), Cl(2)–Pd(2)–S(2) 90.51(8), N(8)–Pd(2)–N(9) 89.19(11), N(9)–Pd(2)–S(2) 85.25(8); Pd(3)–Cl(3) 2.3284(10), Pd(3)–N(9) 2.092(3), Pd(3)–N(10) 2.023(3), Pd(3)–S(3) 2.2791(8), N(9)–Pd(3)–Cl(3) 95.65(8), N(10)–Pd(3)–S(3) 85.87(8), N(9)–Pd(3)–N(10) 89.07(11), Cl(3)–Pd(3)–S(3) 89.44(3). (b) Detailed view of the chair conformation for the Pd₃N₃ ring.

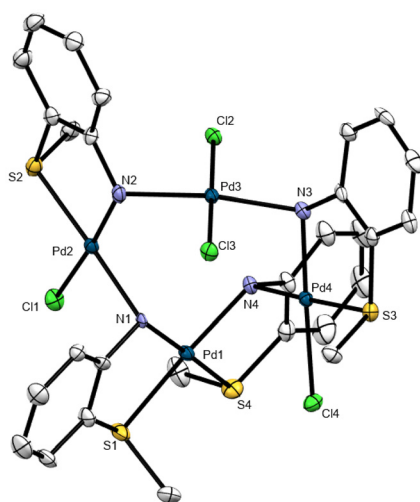


Fig. 4 ORTEP drawing of compound **7** with thermal ellipsoid plot shown at 50% probability level. Hydrogen atoms and solvent molecules have been omitted for clarity. Selected bond distances (Å) and angles (°): Pd(1)–N(1) 2.067(6), Pd(1)–N(4) 2.053(6), Pd(1)–S(1) 2.280(2), Pd(1)–S(4) 2.272(2), N(1)–Pd(1)–S(1) 85.95(16), N(4)–Pd(1)–S(4) 86.22(18), N(1)–Pd(1)–N(4) 95.2(2), S(1)–Pd(1)–S(4) 92.70(8); Pd(2)–N(1) 2.092(6), Pd(2)–N(2) 2.033(7), Pd(2)–S(2) 2.256(2), Pd(2)–Cl(1) 2.330(2), N(1)–Pd(2)–Cl(1) 92.02(17), Cl(1)–Pd(2)–S(2) 88.61(7), N(1)–Pd(2)–N(2) 92.4(2), N(2)–Pd(2)–S(2) 86.92(19); Pd(3)–N(2) 2.046(6), Pd(3)–N(3) 2.055(6), Pd(3)–Cl(2) 2.3156(19), Pd(3)–Cl(3) 2.3261(19), N(2)–Pd(3)–Cl(3) 86.86(19), N(3)–Pd(3)–Cl(2) 87.50(18), N(2)–Pd(3)–Cl(2) 92.85(19), Cl(3)–Pd(3)–N(3) 93.17(18); Pd(4)–N(3) 2.030(6), Pd(4)–N(4) 2.087(6), Pd(4)–S(3) 2.253(2), Pd(4)–Cl(4) 2.3373(19), N(4)–Pd(4)–Cl(4) 91.97(18), Cl(4)–Pd(4)–S(3) 88.60(7), N(3)–Pd(4)–N(4) 92.9(2), N(3)–Pd(4)–S(3) 86.62(19).

as a yellow solid. The ³¹P NMR spectrum displayed two doublets at 26.6 and 6.42 ppm, for the two inequivalent phosphorus nuclei, with the latter one showing the tungsten satellites (¹J_{PW} = 247.9

Hz). The NMR tube solution of **4d** was set aside and left to stand whereupon crystals appeared; the resulting X-ray crystallographic analysis showed them to be quite different from the expected complex, rendering an altogether new compound. The beauty of this serendipitous contingency is that it seems not to be an occasional issue, but rather a repeatable event, *i.e.*, three-fold recrystallization attempts rendered the same structure.

Crystal structure of **8**

Suitable crystals were grown for a chloroform solution of **4d** (Fig. 5 and Table 1). The unit cell consists of one molecule of the compound and two perchlorate anions. The structure depicts a pentanuclear palladium/tungsten *trans*-configured heterometallic linear complex with the metal atoms connected by three linkers: a dppm diphosphine, two acetate anions, and two sulfur-containing aniline molecules stemming from the pincer ligand after hydrolysis of the C=N double bond; no reduction of palladium was observed. The palladium atoms themselves are bridged by two nitrogen atoms: Pd(1)N(1)Pd(2)N(2)Pd(3), from two 2-MeC₆H₄NH₂-N units, and also by two μ-MeCOO-O ligands.⁴⁶ The outer palladium atoms show similar coordination environments each bonded to a chelating [N,S] aniline ligand with the donor atoms in a *cis* geometry; an oxygen donor from the bridging acetate ligand a tungsten metalloligand Ph₂PCH₂P(Ph)₂W(CO)₅, with the nitrogen and phosphorus atoms, on the one hand and the sulfur and oxygen donors, on the other, in *trans* arrangements. The coordination planes at palladium are essentially planar, with slight deviations consequent upon chelation of the aniline moieties. The angles on palladium are *ca.* 90° in the range 89.78–90.22° [Pd(2)], 83.78–95.35° [Pd(1), Pd(3)]. The coordination planes on Pd(1) [Pd(1)N(1)O(7)S(1)P(1)] and Pd(2) [Pd(2)O(8)N(1)O(8)N(1)] are at an angle of 83.68°.



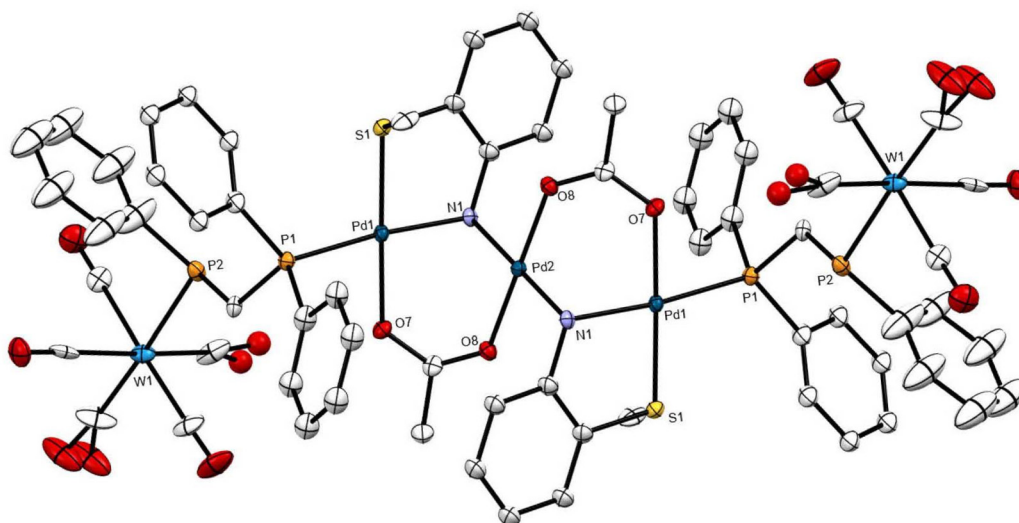


Fig. 5 ORTEP drawing of compound **8** with thermal ellipsoid plot shown at 50% probability level. Hydrogen atoms and solvent molecules have been omitted for clarity. Selected bond distances (Å) and angles (°): Pd(1)–N(1) 2.044(8), Pd(1)–P(1) 2.287(3), Pd(1)–S(1) 2.254(3), Pd(1)–O(7) 2.076(7), Pd(2)–N(1) 2.041(8), Pd(2)–O(8) 1.998(7), N(1)–Pd(1)–S(1) 85.95(16), S(1)–Pd(1)–P(1) 86.22(18), P(1)–Pd(1)–O(7) 95.2(2), O(7)–Pd(1)–N(1) 92.70(8); N(2)–Pd(1)–P(1) 174.0(3), S(1)–Pd(1)–O(7) 177.4(2), N(1)–Pd(2)–O(8) 89.8(3).

Conclusions

In this work we have shown that the reaction conditions for the preparation of cyclometallated compounds from terdentate-[C,N,S] Schiff base ligands have a meaningful effect on the purity of the resulting products. In the case of the lithium metallating agent, the product is obtained in good yield and pure, whereas and in the case of the alternative sodium salt route, needing less restricted reaction conditions, the target compounds are formed but side reactions occur leading to presence of the parent aldehyde after partial decomposition of the organic ligand, as was detected by NMR spectroscopy. Therefore, cleavage of the Schiff base ligand occurs, and the released amine is in turn transformed into a chelating and/or bridging ligand to the metal. Thus, structures with eight- and six-membered rings of alternating palladium and nitrogen atoms are assembled. In either case it was possible to obtain the corresponding triphenylphosphine palladacycles prior abstraction of the chloride ligand. Moreover, thiomethyl aniline itself also shows a unique behavior when reacted with the appropriate palladium(II) reagent yielding a tetranuclear complex containing a Pd₄N₄ eight-membered ring that displays three different varieties of palladium coordination. This finding leads to the conclusion that the behavior previously described stems from a decomposition process which is unique to these iminic palladacycles and not from reaction of the hydrolyzed ligand with unreacted metallating agent. Last, but not least, this more than singular chemical performance of the coordinated Schiff base ligand is evident in the case of the dinuclear Pd/W metallacycle which evolves upon recrystallization to give a *trans*-configured heterometallic mixed valent Pd(II)/W(0) linear complex.

Author contributions

Francisco Reigosa: formal analysis, methodology, conceptualization. Paula Polo: validation, methodology, investigation. Teresa Pereira: conceptualization, methodology. José M. Vila: conceptualization, writing – original draft, supervision, funding acquisition.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was also made possible thanks to the financial support received from the Xunta de Galicia (Galicia, Spain) under the Grupos de Referencia Competitiva Programme (project GRC2019/14). F. R. thanks the Spanish Ministry of Education (grant FPU15/07145).

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