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Chelating or bridging Pd(II) and Pt(II) metalloligands from the functional phosphine ligand *N*-(diphenylphosphino)-1,3,4-thiadiazol-2-amine. New heterometallic Pd(II)/Pt(II) and Pt(II)/Au(I) complexes[†]

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The reaction of two equivalents of the functional phosphine ligand *N*-(diphenylphosphino)-1,3,4-thiadiazol-2-amine Ph₂PNHC=NNCHS (2) with [PdCl₂(NCPh)₂] in the presence of NEt₃ gives the neutral, P,N-chelated complex *cis*-[Pd(Ph₂PN=CNN=CHS)₂] ([Pd(2_{-H})₂], **3b**), which is analogous to the Pt(II) analogue *cis*-[Pt(Ph₂PN=CNN=CHS)₂] ([Pt(2_{-H})₂], **3a**) reported previously. These complexes function as chelating metalloligands when further coordinated to a metal through each of the CH-*N* atoms. In the resulting complexes, each *endo*-cyclic N donor of the thiadiazole rings is bonded to a different metal centre. Thus, the heterodinuclear palladium/platinum complexes *cis*-[Pt(Ph₂PN=CNN=CHS)₂PdCl₂] ([Pt(2_{-H})₂·PdCl₂], **4a**) and *cis*-[Pd(Ph₂PN=CNN=CHS)₂PtCl₂] ([Pd(2_{-H})₂·PtCl₂], **4b**) were obtained by reaction with [PdCl₂(NCPh)₂] and [PtCl₂(NCPh)₂], respectively. In contrast, reaction of **3a** with [AuCl(tht)] occurred instead at the P-bound N atom, and afforded the platinum/digold complex *cis*-[Pt{Ph₂PN(AuCl)=CNN=CHS}₂] ([Pt(2_{-H})₂(AuCl)₂], **5**). For comparison, reaction of **4a** with HBF₄ yielded *cis*-[Pt(Ph₂PNH=CNN=CHS)₂PdCl₂](BF₄)₂ ([H₂**4a**](BF₄)₂, **6**), in which the chelated PdCl₂ moiety is retained. Complexes **3b**, **4a**·CH₂Cl₂, **4b**·0.5C₇H₈, **5**·4CHCl₃ and **6** have been structurally characterized by X-ray diffraction.

Introduction

The synthesis of phosphines containing in addition a nitrogen donor function (P,N ligands) and their transition metal complexes has become increasingly attractive in the last few years owing to their intrinsic properties, considerable structural diversity and broad range of applications.¹ We are interested in oxazoline-and thiazoline-based phosphine systems, such as (2-oxazoline-2-ylmethyl)diphenylphosphine (L_{ox}) and (2-thiazoline-2-ylmethyl) diphenylphosphine (L_{ub}),² which have been successfully applied in several catalytic processes, like some of their derivatives.³



With both L_{ox} and L_{th} , unprecedented tetranuclear complexes [NiCl₂(L)]₄·2CH₂Cl₂ have been structurally characterized, which, in the solid state, undergo an irreversible pressure-induced frag-

mentation into the corresponding mononuclear square planar Ni(II) complexes [NiCl₂(L)] (Scheme 1).⁴ Interestingly, recrystallization of the latter from CH_2Cl_2 -pentane regenerates the tetranuclear complex.



For comparative purposes, we replaced the PCH₂ group of L_{th} with the isoelectronic PNH group and began to examine the coordination properties of *N*-(diphenylphosphino)-thiazolin-2-amine Ph₂PNHC=NCH₂CH₂S (1) (Scheme 2).⁵ Complexes with ligand 1 have shown a higher sensitivity towards hydrolysis or alcoholysis of the P–N bond compared to the P–C bond of L_{th} . However, facile deprotonation in the α -position to the P atom leads to 3 electron donor *P*,*N*-chelates with enhanced chemical persistency compared to their precursors. Thus, reaction of 1 with [PtCl₂(NCPh)₂] in the presence of NEt₃ gives the neutral complex

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cis-[Pt(Ph₂PN=CNCH₂CH₂S)₂] (cis-[Pt(1_{-H})₂]) (Scheme 2). This complex is luminescent and showed an interesting solvent-induced emission enhancement in the solid state when exposed to alcohols, which interact by H-bonding with the P–N nitrogen atoms.⁶

Reactions of *cis*-[Pt(1_{-H})₂] with the organic electrophile EtN=C=S and the monovalent cations Cu⁺, Ag⁺ and Au⁺, as inorganic electrophiles, occurred at one or both electron-rich P-bound N atoms, respectively. With the latter reagents, the complexes isolated were polymeric in the case of [Cu{Pt(1_{-H})₂}(PF₆)]_w⁻⁷ and [Ag{Pt(1_{-H})₂}(OTf)]_w, or molecular in the case of [Pt(1_{-H})₂AuCl] and [Pt(1_{-H})₂(AuCl)₂]. When the thiazoline ring in *cis*-[Pt(1_{-H})₂] was replaced with aromatic thiazole, thiadiazole or benzothiazole, the corresponding metalloligands qualitatively showed slower reactions towards d¹⁰ cations, and the resulting heterometallic complexes were found to be less stable.⁶

Since the P-bound N atoms in $cis-[Pt(1_{-H})_2]$ represented the dominating reaction sites towards electrophiles so far, we wished to introduce an additional function to expand the coordination properties of such metalloligands. We shall see that replacing ligand 1 with N-(diphenylphosphino)-1,3,4-thiadiazol-2-amine (2) resulted in the new P,N-chelated complex cis- $[Pd(Ph_2PN=CNN=CHS)_2]$ (*cis*- $[Pd(\mathbf{2}_{-H})_2]$, **3b**), which should behave as a N, N-chelating metalloligand (Scheme 3), owing to the favourable position of the additional, non coordinated CH-nitrogen atom of each of the thiadiazole rings and the suitable orientation of their lone pairs. This would lead to a κ^2 -*P*,*N*-chelating/ μ -*N*,*N*-bridging mode for ligand $\mathbf{2}_{-H}$. A similar behaviour should be anticipated for its Pt(II) analogue cis- $[Pt(Ph_2PN=CNN=CHS)_2]$ (*cis*- $[Pt(\mathbf{2}_{-H})_2]$, **3a**).⁶ Although doubly bridged thiadiazole dinuclear compounds have already been reported in the 1970s,⁸ to the best of our knowledge only a few heterometallic complexes have been characterized.9 Herein, we examine the reactivity of this N,N function and report new heterometallic complexes in which the thiadiazole moieties form a double bridge.



Results and discussion

The Pd(II) complex cis-[Pd(Ph₂PN=CNN=CHS)₂] (cis-[Pd(2_{-H})₂], **3b**) has been obtained by a 2:1 reaction of Ph₂PNHC=NNCHS (2)⁶ with [PdCl₂(NCPh)₂] in the presence of NEt₃ at room temperature (Scheme 3). Complex **3b** was easily

purified by taking advantage of its poor solubility in MeCN and it was characterized by X-ray diffraction (Fig. 1).



Fig. 1 An ORTEP view of the molecular structure of compound 3b. Hydrogen atoms and solvent molecules omitted for clarity. Ellipsoids include 30% of the electron density. Only one of the two independent molecules is shown (A). Selected distances (Å) and angles (deg), molecule A: P1–Pd1 2.2675(12), P2–Pd1 2.2626(11), N2–Pd1 2.081(3), N5–Pd1 2.083(3), N1–P1 1.660(4), N4–P2 1.662(4), N2–N3 1.370(4), N5–N6 1.384(4), C1–N1 1.305(5), C1–N2 1.351(5), C15–N4 1.324(5), C15–N5 1.345(5), C2–N3 1.271(5), C16–N6 1.277(6); P2–Pd1–P1 102.44(4), N5–Pd1–P2 79.52(9), N2–Pd1–P1 79.52(10), N2–Pd1–N5 98.53(13).

In the molecular structure of **3b**, two almost identical deprotonated ligands, $\mathbf{2}_{\text{H}}$, chelate the metal centre through their phosphorus atoms P1 and P2, and the sp²-hybridized nitrogen atoms N2 and N5, respectively. This structure is analogous to that of the related Pt(II) bischelated complex [Pt($\mathbf{2}_{\text{-H}}$)₂] (**3a**).⁶ The bonds N1–C1/N4–C15 and C1–N2/C15–N5 are longer than a double bond and shorter than a single bond, respectively, indicating electronic delocalization over the NCN system (for convenience, we represent the N1–C1 and N4–C15 bonds by formal double bonds in the schemes).

In solution, the ³¹P{¹H} NMR spectrum of **3b** shows a singlet at 90.9 ppm, whereas the ¹H NMR spectrum shows a complicated filled-in doublet signal for the protons H2 and H16, bound to C2 and C16, respectively, which consists of five peaks. This multiplet could be simulated by considering two ⁵⁺⁶*J*(H,P) values of 3.6 Hz and 1.4 Hz for the coupling between H2,P1 and H2,P2, respectively, and a small ²*J*(P,P) *cis*-coupling of 0.7 Hz. A similar situation will be encountered below with **4a** (Fig. 6).

The coordination chemistry of systems in which two pyrazolyl groups are linked by a spacer X (Scheme 4) through one nitrogen atom of each pyrazole ring and behave as N,N chelates have been much studied.¹⁰ Such ligands usually readily readily react with Pd(II) or Pt(II) precursors to give [Pd(N,N)Cl₂] or [Pt(N,N)Cl₂] chelate complexes (Scheme 4).¹¹

Complexes **3a** and **3b** were reacted with $[PdCl_2(NCPh)_2]$ and $[PtCl_2(NCPh)_2]$ in a toluene– CH_2Cl_2 mixture under



Scheme 4 X = organic or organometallic group, M = Pd(II) or Pt(II).

reflux to give the heterobimetallic Pt(II)/Pd(II) complexes *cis*-[Pt(Ph₂PN=CNN=CHS)₂PdCl₂] ([Pt(2_{-H})₂·PdCl₂], **4a**) (Scheme 5, Fig. 2) and *cis*-[Pd(Ph₂PN=CNN=CHS)₂PtCl₂] ([Pd(2_{-H})₂·PtCl₂], **4b**) (Scheme 5, Fig. 4), respectively.







Fig. 2 An ORTEP view of the molecular structure of 4a in $4a \cdot CH_2CI_2$. Hydrogen atoms and solvent molecules have been omitted for clarity. Ellipsoids include 40% of the electron density. Selected distances (Å) and angles (deg): P1–Pt1 2.2512(11), P2–Pt1 2.2469(11), N5–Pt1 2.072(3), N2–Pt1 2.065(3), N3–Pd1 2.056(3), N6–Pd1 2.040(3), Pd1–Cl1 2.2754(11), Pd1–Cl2 2.2779(11), N1–P1 1.671(4), N4–P2 1.676(4), N2–N3 1.383(5), N5–N6 1.371(5), C1–N1 1.297(6), C1–N2 1.359(5), C15–N4 1.291(5), C15–N5 1.371(5), C2–N3 1.292(5), C16–N6 1.298(6); P2–Pt1–P1 103.46(4), N5–Pt1–P2 79.84(10), N2–Pt1–P1 80.25(10), N2–Pt1–N5 96.27(14), N6–Pd1–N3 94.43(13), N3–Pd1–Cl1 88.52(10), N6–Pd1–Cl2 88.07(10), C11–Pd1–Cl2 89.03(4).

In the molecular structure of the bimetallic complex 4a in 4a·CH₂Cl₂, the metalloligand 3a chelates the Pd(II) centre through N3 and N6, which are in a mutual cis arrangement. Although the Pt(II) centre is not located on a symmetry element, the two chelating moieties have very similar bonding characteristics. Both metals feature a slightly distorted square planar environment. The N1-C1 and C1-N2 (likewise the N4-C15 and C15-N5) bond lengths are not significantly different from the corresponding bonds in the parent complex 3a. However, a major difference between them stems from the orientations of the chelating ligands. In 3a, the complex shows a planar structure (excluding the phenyls), whereas in 4a, the mean planes formed by C1, N2, N3, C2, S1 and C15, N5, N6, C16, S2 form an angle of 33.3(1)°. The resulting orientation of the lone pairs at N3 and N6 and the non-coplanarity of the PdCl₂ group with the Pt mean that the coordination plane [angle between the Pt1, P1, P2, N2, N5 and Pd1, N3, N6, Cl1, Cl2 planes: 38.21(6)°] allows a minimization of the steric repulsions between the chlorides and the neighbouring CH groups (Fig. 3). The N3...N6 separation of 3.006(5) Å is comparable to that in the parent complex 3a [3.011(4) Å and 3.057(4), two crystallographically independent molecules were present].6



Fig. 3 An ORTEP side view of the molecular structure of **4a** in **4a** \cdot CH₂Cl₂. Hydrogen atoms, phenyls and solvent molecules have been omitted for clarity, except for the H atoms in proximity to the two chlorides. Ellipsoids include 40% of the electron density.

The structure of **4b** is analogous to that of **4a**, the Pt(II) and Pd(II) centres having exchanged positions (Fig. 4). The angles of $32.8(4)^{\circ}$ between the planes of the two thiadiazole rings and of $36.3(2)^{\circ}$ between the Pd1, P1, P2, N2, N5 and Pt1, N3, N6, Cl1, Cl2 planes are only slightly smaller than in **4a**. The N3–N6 distance of 3.058(5) Å in **3b** is only slightly longer than that in **4b** [2.999(9) Å]. The similarities between the two structures reflect the similar covalent radii of the two metal centres, that of Pt (1.36 Å) being only slightly smaller than that of Pd (1.39 Å).¹²

Pairs of molecules of **4b** are disposed centrosymmetrically to form pseudo-dimers through multiple non-classical H-bonds¹³ between the two coordinated chlorides and the thiadiazole protons (Fig. 5).

In view of the surprisingly severe thermal conditions required for the synthesis of **4a** and **4b**, when considering the usually facile substitution reactions of $[MCl_2(NCPh)_2]$ (M = Pd, Pt), and the lack of reaction at room temperature of **3a** with $[Pd(NCMe)_4]^{2+}$ or $[Cu(NCMe)_4]^+$ in CH_2Cl_2 , it is reasonable to suggest that the nature of the spacer X (Scheme 4) significantly influences the reactivity



Fig. 4 An ORTEP view of the molecular structure of compound 4b in 4b- $0.5C_7H_8$. Hydrogen atoms and solvent molecules have been omitted for clarity. Ellipsoids include 40% of the electron density. Selected distances (Å) and angles (deg): P1–Pd1 2.2639(19), P2–Pd1 2.267(2), N5–Pd1 2.068(5), N2–Pd1 2.079(6), N3–Pt1 2.045(6), N6–Pt1 2.036(6), Pt1–Cl1 2.278(2), Pt1–Cl2 2.2900(18), N1–P1 1.662(6), N4–P2 1.666(6), N2–N3 1.379(7), N5–N6 1.352(7), C1–N1 1.311(8), C1–N2 1.345(9), C15–N4 1.315(9), C15–N5 1.355(10), C2–N3 1.281(9), C16–N6 1.280(9); P2–Pd1–P1 103.42(7), N5–Pd1–P2 80.72(18), N2–Pd1–P1 80.91(16),N2–Pd1–N5 94.7(2), N6–Pt1–N3 94.7(2), N3–Pt1–Cl1 88.82(18), N6-Pt1-Cl2 88.46(16), C11-Pt1-Cl2 88.19(7).



Fig. 5 A diagram of the solid-state structure of **4b** in **4b** $\cdot 0.5C_7H_8$ showing the pseudo-dimers formed by multiple non-classical H-bonds. Hydrogen atoms and solvent molecules have been omitted for clarity, except for the H atoms of the thiadiazole rings. Contacts between these atoms and the coordinated chlorides are depicted as dashed lines (H · · · Cl distances \leq 2.9 Å).

of the uncoordinated N–N atoms of **3a,b** and thus the propensity of these metalloligands to function as N,N-chelates toward Pd(II) and Pt(II) precursors. This is most probably related to the rigidity of the [Pt(P,N)₂] and [Pd(P,N)₂] moieties in **3a** and **3b** and to the steric hindrance generated by the C16–H and C2–H protons. The similarities between the N···N separations in **3a**/4**a** and **3b**/4**b** suggest that a significant increase in this separation is not required to accommodate the second metal between these donor atoms. Thus, the high kinetic barrier to N,N-chelation of **3a,b** results from the necessary folding of their structure to allow coordination of a metal centre to N3 and N6.

In solution, the two heterobimetallic complexes show NMR spectra that are fully consistent with their solid state structure. In the ³¹P{¹H} NMR spectrum of **4a**, the phosphorus nuclei resonate at 62.8 ppm, and show ¹⁹⁵Pt satellites with a ¹J(³¹P,¹⁹⁵Pt) coupling constant of 3420 Hz, consistent with the *trans* influence exerted by the N atoms.^{6,14} The pattern of the ¹H NMR resonance for the H2 and H16 protons is a filled-in doublet at 8.92 ppm (Fig. 6), significantly low-field shifted when compared to that of **3a** (8.26 ppm),⁶ as a result of the proximity of the PdCl₂ group. A similar trend is observed for **4b**, whose H2 and H16 protons resonate at 8.83 ppm (8.11 ppm in **3b**). The ³¹P{¹H} singlets of **4a** (62.8 ppm) and **4b** (84.7 ppm) are slightly deshielded, by a similar value, when compared to those of the precursor complexes **3a** (69.6 ppm) and **3b** (90.9 ppm).



Fig. 6 Experimental (top) and simulated (bottom) ¹H NMR spectra of **4a** in the region of the resonance of protons H2 and H16 centered at 8.92 ppm.

Although diazole and thiadiazole doubly bridged dinuclear compounds are fairly common, no example of structurally characterized heterometallic palladium–platinum complexes appears to have been reported in the literature.¹⁵ Only one example was found, in which a diazole ligand bridges these two metals.¹⁶

Since complex **4a** could, in principle, still be used as a bimetalloligand (*via* the P–N and/or the S donors), we attempted to coordinate a third metal, by reacting **4a** with [AuCl(tht)] (tht = tetrahydrothiophene). Although the latter readily reacted with the nitrogen atoms in the α -position to phosphorus, expulsion of the PdCl₂ moiety from the complex, in the form of [PdCl₂(tht)₂], was concomitantly observed with the formation of *cis*-[Pt{Ph₂PN(AuCl)=CNN=CHS}₂] ([Pt(**2**_{-H})₂·(AuCl)₂], **5**) (Fig. 7, Scheme 6).

Unlike 4a, complex 5 is not stable in solution and releases metallic gold with reformation of 3a. Complex 5 was also prepared by direct reaction of [AuCl(tht)] with 3a. Reactions of 3a or 3b with [AuCl(tht)] never allowed characterization of a complex showing coordination of the sulfur atom to gold, which suggests that this sulfur would be a weaker donor than that of tht, consistent with the aromaticity of the thiadiazole ring.



Fig. 7 An ORTEP view of the molecular structure of 5 in 5.4CHCl₃. Hydrogen atoms and solvent molecules have been omitted for clarity. Ellipsoids include 40% of the electron density. Selected distances (Å) and angles (deg): Pt1–P1 2.2383(16), Pt1–P2 2.2469(15), Pt1–N5 2.063(5), Pt1–N2 2.070(5), Au1–N1 2.014(5), Au1–Cl1 2.2431(19), Au2–N4 2.014(5), Au2–Cl2 2.2394(16), P1–N1 1.700(5), P2–N4 1.707(5), N1–Cl 1.339(9), N2–Cl 1.353(8), N2–N3 1.382(8), N3–C2 1.275(9), S1–C1 1.708(6), S1–C2 1.743(9), N4–Cl5 1.337(8), N5–Cl5 1.342(8), N5–N6 1.387(7), N6–Cl6 1.292(8), S2–Cl5 1.720(6), S2–Cl6 1.746(7); P1–Pt1–P2 99.33(6), N5–Pt1–N2 98.4(2), N2–Pt1–P1 81.13(15), N5–Pt1–P2 81.11(14), N1–Au1–Cl1 177.08(17), N4–Au2–Cl2 178.38(15).



In the molecular structure of **5** in **5**·4CHCl₃, **3a** acts as a bidentate bridging metalloligand, coordinating two AuCl units through N1 and N4. The bond lengths around Pt are analogous to those found in **4a**. Compared to the corresponding bond

Table 1A comparison of selected bond distances (Å) between complexes3a, 4a and 6, together with a common atom numbering scheme



`М́						
	Complex 3a	Complex 4a	$\frac{\text{Complex } 6}{\text{M} = \text{PdCl}_2}$			
	$\overline{\mathbf{M} = \text{nothing}}$	$\mathbf{M} = \mathbf{PdCl}_2$				
Pt1–P1	2.2560(9)	2.2512(11)	2.241(3)			
Pt1–P2	2.2502(8)	2.2469(11)	2.230(3)			
Pt1–N2	2.076(3)	2.065(3)	2.074(3)			
Pt1–N5	2.078(3)	2.072(3)	2.063(9)			
P1-N1	1.661(3)	1.671(4)	1.724(4)			
P2-N4	1.672(3)	1.676(4)	1.708(4)			
Pd1–N3	_	2.056(3)	2.056(9)			
Pd1–N6		2.040(3)	2.051(10)			
Pd1–Cl1		2.2754(11)	2.272(3)			
Pd1–Cl2		2.2779(11)	2.288(3)			
C1-N1	1.311(5)	1.297(6)	1.315(14)			
C15–N4	1.310(5)	1.291(5)	1.305(15)			
C1-N2	1.365(4)	1.359(5)	1.352(14)			
C15–N5	1.352(4)	1.371(5)	1.323(14)			
N2-N3	1.380(4)	1.383(5)	1.370(13)			
N5–N6	1.371(4)	1.371(5)	1.376(13)			

distances in **3a** (Table 1), the N1–C1 and C1–N2 distances, and the related N4–C15 and C15–N5, are slightly longer and shorter, respectively. This may indicate a more delocalized N....C...N π system. Related Pd–Au complexes have been prepared by reaction of a cyclometallated phosphinoenolate or phosphinoiminolate Pd(II) complex, respectively, with a Au(I) reagent which binds to the carbon or nitrogen atom, respectively, in α -position to the phosphorus donor (Scheme 7).^{17,18}



The lengths of the Au–Cl [2.2431(19) and 2.2394(16) Å] and Au–N [2.014(5) Å] bonds compare well with those reported for analogous phosphino-thiazoline Pt(II)/Au(1) bimetallic complexes.⁶ Excluding the phenyl groups, the complex shows a planar structure (maximum deviation from the mean plane: 0.089(9) Å for C2), contrasting with **4a**.

Despite the instability of **5**, we were able to record NMR data. Its ${}^{31}P{}^{1}H$ NMR spectrum consists of a singlet at 77.5 ppm, slightly deshielded when compared to that of **3a**, whereas, the diagnostic H2 and H16 protons undergo a low-field shift (from 8.26 to 8.47 ppm), suggesting a rather pronounced electronic communication between the P-nitrogen atoms and the C2 and C16 carbons.

We first hypothesized that the AuCl coordination-induced expulsion of the $PdCl_2$ fragment could stem from electronic factors, the electron density at N3 and N6 being reduced upon coordination of N1 and N4 to an electrophile. However, when **4a** was reacted in an NMR tube with two equivalents of tht, the ligand associated with the Au(I) reagent, the mononuclear Pt complex

3a formed within a few minutes (with ${}^{31}P{}^{1}H{}$ monitoring). This was rather surprising, since a formally bisimine chelating ligand, such as in 4a, was thought to be more efficient towards Pd(II) than the labile tht. Formation of 3a from 4a and tht suggests that steric factors play an important role in this reaction, and that the tension of the metalloligand 3a within 4a (exemplified by its bent arrangement) could labilize the structure, promoting the expulsion of PdCl₂. On the other hand, upon incorporation of the AuCl fragments, the system seems to lose stability since, as mentioned above, complex 5 is an unstable product. With the aim to introduce a PdCl₂ moiety into 5 by formation of an N,N-chelate, 5 was reacted with [PdCl₂(cod)], rather than [PdCl₂(NCPh)₂] because the liberated cod would be easier to remove from the reaction mixture than benzonitrile, thus preventing the type of competition reactions encountered in the Au/tht system. However, our attempts failed, owing to the high kinetic barrier to the N,Nchelation of 5, similar to that of 3a (see above), which requires the use of thermal conditions incompatible with the instability of 5.

To confirm that cis-[Pt(Ph₂PN=CNN=CHS)₂PdCl₂] (4a) is still an electron-rich species, we reacted it with HBF₄·Et₂O, both in solution and in the solid state. This resulted in a rapid and clean double protonation of the P-bound nitrogen atoms and the formation of very stable cis-[Pt(Ph₂PNH=CNN=CHS)₂ PdCl₂](BF₄)₂ (4a·2HBF₄, 6, Fig. 8, Scheme 8), which retains the PdCl₂ group. In view of the isolobal analogy between the proton and a [R₃P-Au]⁺ cation,¹⁹ this indicates that the use of 4a as metalloligand for the formation of trimetallic, tetranuclear complexes should, in principle, be possible but intrinsic difficulties remain to be overcome.

N1

N2

Pd1

CI1





Scheme 8 The localization of the NH=C double bonds has a formal character.

In the molecular structure of **6**, the N atoms are all engaged as donors. Metalloligand **3a** chelates a $PdCl_2$ unit as in **4a** and is doubly protonated on both P-bound nitrogen atoms. These NH functions are involved in H-bonds with the neighbouring BF_4^- counter ions. Protonation on N1 and N4 results in longer P–N distances than in its parent complex **4a**, suggesting that their lone pair in **4a** is partly engaged in this bond. The Pt–P and Pd–Cl distances remain similar. Other distances cannot be reliably compared, due to the relatively high standard deviations for the bond lengths in **6**. Selected bond distances are compared in Table 1.

Conclusion

The multidentate, functional phosphine ligand 2 has proven to be efficient in coordination chemistry and owing to the presence of a P-bound NH group, it readily forms in the presence of NEt₃, a stable bischelated palladium(II) complex 3b, in which 2 has been deprotonated at the N atom. In both 3b and its previously reported Pt(II) analogue 3a, the *cis*-arrangement around the d⁸ metal centres provides a potentially N.N-chelating system involving the CH-N nitrogen of each of the thiadiazole ring. This has been exploited with Pd(II) and Pt(II) precursors to form the heterobimetallic complexes 4a and 4b, respectively, in which ligand 2 behaves as an anionic, formally 6e⁻ donor. Attempts to increase the ligand donicity and prepare tetranuclear, trimetallic Pd(II)/Pt(II)/Au(I) complexes failed, since 4a and 4b were found to be labile when exposed to tht, which is the ligand associated with the Au(I) reagent. This resulted in the loss of the MCl₂ moiety. However, 4a was successfully protonated to give a stable cationic Pt(II)/Pd(II) complex, suggesting that 2 could indeed be used as an anionic ligand, formally donating 8e⁻.

Experimental section

General considerations

All manipulations were carried out under an inert argon atmosphere, using standard Schlenk line conditions and dried and freshly distilled solvents. Unless otherwise stated, the ¹H, ¹³C{¹H} and³¹P{¹H} NMR spectra were recorded on a Bruker Avance 300 instrument at 300.13, 75.47, and 121.49 MHz, respectively, using TMS or H₃PO₄ (85% in D₂O) as the external standards, with downfield shifts reported as positive. All NMR spectra were measured at 298 K, unless otherwise specified. The assignment of the signals was made by ¹H, ¹H-COSY, and ¹H, ¹³C-HMQC, ¹³C-HSQC experiments. Elemental C, H, and N analyses were performed by the Service de Microanalyses, Université de Strasbourg (France).

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Ligand 2^6 and the complexes [PtCl₂(NCPh)₂], [PdCl₂(NCPh)₂],²⁰ [AuCl(tht)] (tht = tetrahydrothiophene)²¹ and $3a^6$ were prepared according to literature procedures. Ph₂PCl and NEt₃ were freshly distilled before use. Other chemicals were commercially available and were used as received.

Preparation and spectroscopic data for 3b

To a stirred solution of $[PdCl_2(NCPh)_2]$ (0.200 g, 0.52 mmol) in MeCN (100 mL), NEt₃ (0.500 mL, 3.59 mmol) and solid **2** (0.300 g, 1.05 mmol) were added. Stirring was continued for 1 h and Et₃N·HCl was removed by filtration. The volatiles were removed under reduced pressure and the white powder obtained was washed with MeCN (3 × 10 mL). Drying under reduced pressure gave pure **3b** as a white powder. Yield: 0.327 g, 93%. ¹H NMR (CD₂Cl₂): δ = 7.13–7.39 (m, 20H, Ph), 8.11 (filled-in doublet simulated as AA'XX' spin system, 2H, ⁵⁺⁶J(H,P) = 3.6 and 1.4 Hz, ²J(P,P) = 0.7 Hz, N==CH); ³¹P{¹H} NMR (CD₂Cl₂): δ = 90.9 (s); ¹³C{¹H} NMR (CD₂Cl₂): δ = 128.2–132.5 (m, Ph), 139.2 (br, N==CH, ⁴J(CP) = 6.4 Hz), 184.5 (N=C==N, indirect observation by HMBC). Anal. calcd for **3b**: C 49.82, H 3.29, N 12.45. Found: C 49.61, H 3.40, N 12.57.

Preparation and spectroscopic data for 4a

Solid [PdCl₂(NCPh)₂] (0.061 g, 0.157 mmol) was added to a solution of complex 3a (0.120 g, 0.157 mmol) in a mixture of CH₂Cl₂ (20 mL)/toluene (60 mL). The resulting slurry was stirred under reflux for 3 h. The solution was cooled to room temperature, the volatiles were removed under reduced pressure and the residue was washed with CH_2Cl_2 (3 × 10 mL), and evaporation of the volatiles gave compound 4a as an orange powder. Yield: 0.130 g, 88%. The product can be recrystallized by layering toluene onto a saturated solution of complex 4a in CH₂Cl₂. ¹H NMR (CD₂Cl₂): δ = 7.19–7.45 (m, 20H, Ph), 8.92 (filled-in doublet simulated as a AA'XX' spin system, 2H, ${}^{5+6}J(H,P) = 3.6$ and 1.9 Hz, ${}^{2}J(P,P) =$ 0.8 Hz, N=CH); ${}^{31}P{}^{1}H$ NMR (CD₂Cl₂): $\delta = 62.8$ (s, with Pt satellites, ${}^{1}J({}^{31}P, {}^{195}Pt) = 3420 \text{ Hz}$; ${}^{13}C\{{}^{1}H\} \text{ NMR } (CD_{2}Cl_{2})$: $\delta =$ 128.1-132.4 (m, Ph), 151.5 (br, N=CH), 183.2 (N-C=N, indirect observation by HMBC). Anal. calcd for 4a·CH₂Cl₂: C 33.95, H 2.36, N 8.19. Found: C 34.22, H 2.30, N 7.87.

Preparation and spectroscopic data for 4b

The procedure described for complex **4a** was also applied to the synthesis of **4b**, by using [PtCl₂(NCPh)₂] (0.100 g, 0.212 mmol) and **3b** (0.143 g, 0.212 mmol). Yield: 0. 170 g, 85%. ¹H NMR (CDCl₃): $\delta = 7.12-7.37$ (m, 20H, Ph), 8.83 (filled-in doublet simulated as a AA'XX' spin system, 2H, ⁵⁺⁶*J*(H,P) = 3.4 and 1.4 Hz, ²*J*(P,P) = 0.4 Hz, N=CH); ³¹P{¹H} NMR (CDCl₃): $\delta = 84.7$ (s); ¹³C{¹H} NMR (CDCl₃): $\delta = 128.1-132.4$ (m, Ph), 149.4 (br, N=CH), 178.8 (N-C=N, indirect observation by HMBC). Anal. calcd for **4b**·1.5CH₂Cl₂: C 33.16, H 2.36, N 7.87. Found: C 33.18, H 2.67, N 7.79.

Observation and crystallization of 5

(a) In a 1 cm diameter NMR tube, solid complex **4a** (0.050 g, 0.053 mmol) was dissolved in $CDCl_3$ (5 mL). Solid [AuCl(tht)] (0.033 g, 0.106 mmol) was added to this solution. After 10 min,

quantitative formation of **5** was spectroscopically observed. Although a gold mirror progressively formed, few crystals suitable for X-ray analysis were obtained by layering the CDCl₃ solution with Et₂O. A direct synthesis of this complex is detailed below, see (b). ¹H NMR (CDCl₃): δ = 7.15–7.55 (m, 20H, Ph), 8.47 (m simulated as a AA'XX' spin system, 2H, ⁵⁺⁶*J*(H,P) = 4.5 Hz, ²*J*(P,P) = 5.2 Hz, N==CH); ³¹P{¹H} NMR (CDCl₃): δ = 77.5 (s, with Pt satellites, ¹*J*(P,Pt) = 3328 Hz); ¹³C{¹H} NMR (CDCl₃): δ = 128–133 (m, Ph), 142.7 (br, N==CH), 187.6 (s, N–C==N).

(b) Solid [AuCl(tht)] (0.064 g, 0.200 mmol) was added to a solution of complex **3a** (0.076 g, 0.100 mmol) in CH_2Cl_2 (10 mL). The resulting reaction mixture was stirred for 5 min and then precipitated with pentane (100 mL). The solid was collected by filtration and washed with pentane (2 × 10 mL). Evaporation of the volatiles afforded **5** as a white powder. Yield: 0.122 g, 89%. Anal. calcd for **5**: C 27.37, H 1.81, N 6.84. Found: C, 29.50, H, 2.02, N 6.10.

Preparation and spectroscopic data for 6

(a) In a 5 mm NMR tube, a solution of HBF₄·Et₂O (0.006 g, 0.037 mmol) was added to a CDCl₃ solution (0.5 mL) of **4a** (0.016 g, 0.017 mmol). After 10 min, the NMR signals of **4a** have disappeared and a precipitate formed. The volatiles were removed under reduced pressure and CD₃CN was added, which dissolved the precipitate. Complex **6** was observed spectroscopically and suitable crystals for X-ray diffraction were obtained by layering diethyl ether onto this saturated solution of complex **6** in CD₃CN. ¹H NMR (CD₃CN): $\delta = 7.34-7.63$ (m simulated as a AA'XX' spin system, 20H, Ph), 9.02 (m, 2H, ⁵⁺⁶*J*(H,P) = 1.8 and 1.9 Hz, N=CH); ³¹P{¹H} NMR (CD₃CN): $\delta = 67.1$ (s, with Pt satellites, ¹*J*(³¹P,¹⁹⁵Pt) = 3415 Hz).

(b) A solution of HBF₄·Et₂O (0.035 g, 0.216 mmol) was added to a stirred solution of **4a** (0.100 g, 0.106 mmol) in CH₂Cl₂ (10 mL). Stirring was continued for 10 min, the volatiles were removed under vacuum and the residue was washed with diethyl ether (2 × 10 mL). The resulting residue was dissolved in a minimum amount of acetonitrile and the solution was layered with diethyl ether, giving yellow microcrystals of **6** (Yield: 0.087 g, 73%). Anal. Calcd for **6**: C 30.12, H 2.17, N 7.53. Found: C 29.71, H 2.35, N 7.75.

Crystal structure determinations

Suitable crystals for the X-ray analysis of all compounds were obtained as described above. The intensity data were collected on a Kappa CCD diffractometer²² (graphite monochromated Mo-K α radiation, $\lambda = 0.71073$ Å) at 173(2) K. Crystallographic and experimental details for the structures are summarized in Table 2. The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares procedures (based on F^2 , SHELXL-97)²³ with anisotropic thermal parameters for all the non-hydrogen atoms. The hydrogen atoms were introduced into the geometrically calculated positions (SHELXS-97 procedures) and refined riding on the corresponding parent atoms. In $4b \cdot 0.5C_7H_8$, a molecule of toluene was found disordered over two positions around the symmetry centre. It was refined with restrained anisotropic parameters. In 5.4CHCl₃, a chloroform molecule was found disordered in two positions with no atom in common and with equal occupancy factors. The disorder was

	3b	$4a \cdot CH_2Cl_2$	$\textbf{4b}{\cdot}\textbf{0.5C}_{7}\textbf{H}_{8}$	5-4CHCl ₃	6
Chemical formula	$C_{28}H_{22}N_6P_2PdS_2$	$\begin{array}{c} C_{28}H_{22}Cl_2N_6P_2PdPtS_2 \cdot \\ CH_2Cl_2 \end{array}$	$C_{28}H_{22}Cl_2N_6P_2PdPtS_2$ 0.5(C ₇ H ₈)	$\begin{array}{c} C_{28}H_{22}Au_2Cl_2N_6P_2PtS_2 \\ 4(CHCl_3) \end{array}$	$\frac{C_{28}H_{24}Cl_2N_6P_2PdPtS_2}{2(BF_4)}$
Formula mass	674.98	1025.89	987.03	1705.97	1116.60
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic	Monoclinic
a/Å	11.3926(4)	10.2464(4)	9.9144(3)	10.9741(5)	14.5753(8)
b/Å	14.0042(4)	19.2382(8)	13.1141(3)	13.6758(9)	13.1508(8)
c/Å	18.9125(8)	19.7126(6)	13.9616(3)	17.5503(9)	21.3008(9)
α (°)	99.963(2)	90.00	111.536(1)	89.302(5)	90.00
β (°)	91.366(2)	120.504(2)	102.871(1)	73.211(5)	92.351(3)
γ (°)	109.306(2)	90.00	91.897(1)	80.247(2)	90.00
$V/Å^3$	2794.08(17)	3348.0(2)	1632.85(7)	2483.3(2)	4079.4(4)
T/K	173(2)	173(2)	173(2)	173(2)	173(2)
Space group	$P\overline{1}$	P21/c	$P\overline{1}$	$P\overline{1}$	P21/c
Ź	4	4	2	2	4
μ/mm^{-1}	0.959	5.283	5.254	9.638	4.244
Measd. Refl.	11 343	31 573	11 407	28 663	7937
Indep. refl.	11 343	9783	7496	14 475	7937
R _{int}	0.0533	0.0576	0.0376	0.0570	0.0000
$R_1(I > 2\sigma(I))$	0.0441	0.0392	0.0482	0.0472	0.0670
$wR(F^2)$ $(I > 2\sigma(I))$	0.0907	0.0711	0.0967	0.1036	0.1725
R_1 (all data)	0.0835	0.0746	0.0942	0.0800	0.1094
$wR(F^2)$ (all data)	0.1062	0.0802	0.1148	0.1179	0.1905
S on F^2	1.026	0.986	1.022	0.999	1.024

 Table 2
 X-ray data collection and refinement parameters

modelled unrestrained. The crystals of **6** were of poor quality and visibly twinned. In addition, badly disordered solvent molecules were found. Attempts to determine these atomic positions failed. A PLATON–SQUEEZE procedure was then applied.²⁴ The estimation of the missing electron count was 379 in 651 Å³. This is consistent with 2 Et₂O molecules per asymmetric unit. The procedure resulted in improved refinement parameters. One of the BF₄ anions was disordered as well. Attempts to model the disorder failed. This anion was then refined with restrained anisotropic parameters, B–F distances and F–B–F angles. CCDC 801707 (**3b**), 801708 (**4a**·CH₂Cl₂), 801709 (**4b**·0.5C₇H₈), 810710 (**5**·4CHCl₃), 801711 (**6**) contain the supplementary crystallographic data for this paper, see ESI.[†]

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