Synthesis of platinum(II) cyclometallated compounds derived from imines containing pyridyl or pyrimidyl groups[1]

Margarita Crespo, Craig M. Anderson, and Joseph M. Tanski

Abstract: The reaction of compounds $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ and *cis*-$[PtPh_2(SMe_2)_2]$ with ligands 4-(2′-C_5H_4N)$C_6H_4CHNCH_2CH_2NMe_2$ (**1a**) and 4-(3′,5′-$C_4H_3N_2$)$C_6H_4CHNCH_2CH_2NMe_2$ (**1b**) carried out in acetone at room temperature produced compounds in which the imines act as bidentate [*N,N*′] ligands. Analogous compounds could be obtained in refluxing methanol when *cis*-$[PtCl_2(DMSO)_2]$ was used as starting material. The corresponding cyclometallation processes leading to platinum(II) compounds with a tridentate [*C,N,N*′] ligand took place under different reaction conditions, except for metallation of **1a** with *cis*-$[PtPh_2(SMe_2)_2]$, which could not be achieved. All compounds were characterized by usual techniques and [PtMe{4-(3′,5′-$C_4H_3N_2$)$C_6H_3CHNCH_2CH_2NMe_2$}] (**3bMe**) was also characterized crystallographically.

Key words: platinum, imines, pyridyl, pyrimidyl, cyclometallation, crystal structure.

Résumé : Opérant en solution dans l'acétone et à la température ambiante on a effectué la réaction des produits $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ et *cis*-$[PtPh_2(SMe_2)_2]$ avec les ligands 4-(2′-C_5H_4N)$C_6H_4CHNCH_2CH_2NMe_2$ (**1a**) et 4-(3′,5′-$C_4H_3N_2$)$C_6H_4CHNCH_2CH_2NMe_2$ (**1b**) et on en a isolé des produits dans lesquels les imines agissent comme des ligands [*N,N*′]-bidentates. On a aussi pu obtenir des composés analogues en opérant dans le méthanol au reflux en présence de *cis*-$[PtCl_2(dmso)_2]$ utilisé comme substrat. Les processus de cyclométallation correspondants qui conduisent à la formation de composés du platine(II) avec un ligand tridentate [*C,N,N*′] se produit aussi dans des conditions réactionnelles différentes, mais la métallation du composé **1a** par le *cis*-$[PtPh_2(SMe_2)_2$ ne peut pas être réalisée. On a caractérisé tous les produits par les techniques usuelles et on a fait appel à la diffraction des rayons X pour caractériser le [PtMe{4-(3′,5′-$C_4H_3N_2$)$C_6H_3CHNCH_2CH_2NMe_2$}] (**3bMe**).

Mots-clés : platine, imines; pyridyle, pyrimidyle, cyclométallatation, structure cristalline.

[Traduit par la Rédaction]

Introduction

Cycloplatinated compounds have been a topic of interest in the last years as a consequence of the wide range of their potential applications in many areas (1–8). In spite of the large number of this type of compound described so far, the factors that control the cyclometallation process are not fully understood. Besides gross electronic and steric factors, subtle differences in the substituents of the ligands to be metallated can be decisive in the course of the reaction (9, 10). Following our studies of cycloplatination of imines containing aromatic groups such as benzene (11, 12), thiophene (13), furane (14), naphthalene (15), phenanthrene and anthracene (16), and biphenyls (17, 18), we now report the reactions of imines derived from 4-(2-pyridyl)benzaldehyde (**1a**) and 5-(4-formylphenyl)pyrimidine (**1b**) with metallating agents $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$, *cis*-$[PtPh_2(SMe_2)_2]$ and *cis*-$[PtCl_2(DMSO)_2]$. The aim of this study is to evaluate the influence of pyridyl or pyrimidyl substituents in the aryl group as well as of the metallating substrate used in the synthesis of novel platinacycles. For all these systems, the labile sulfide or sulfoxide ligands should be easily replaced by the two nitrogen atoms of the ligands leading to isolation of [*N,N*′] coordination compounds. The intramolecular C–H bond activation may occur through either oxidative addition or electrophilic substitution pathways (19). Moreover, the presence of one or two nitrogen atoms in the aromatic moiety introduces reactive sites on the ligands and allows further chemical reactions of the corresponding cyclometallated compounds (20).

Received 1 April 2008. Accepted 23 April 2008. Published on NRC Research Press Web site at canjchem.nrc.ca on 17 July 2008.

We are pleased to contribute this paper to the Special Issue recognizing the outstanding scientific career of Richard J. Puddephatt, who we hold in the highest esteem and continues to influence and inspire our own work.

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[1]This article is part of a Special Issue dedicated to Professor R.J. Puddephatt.

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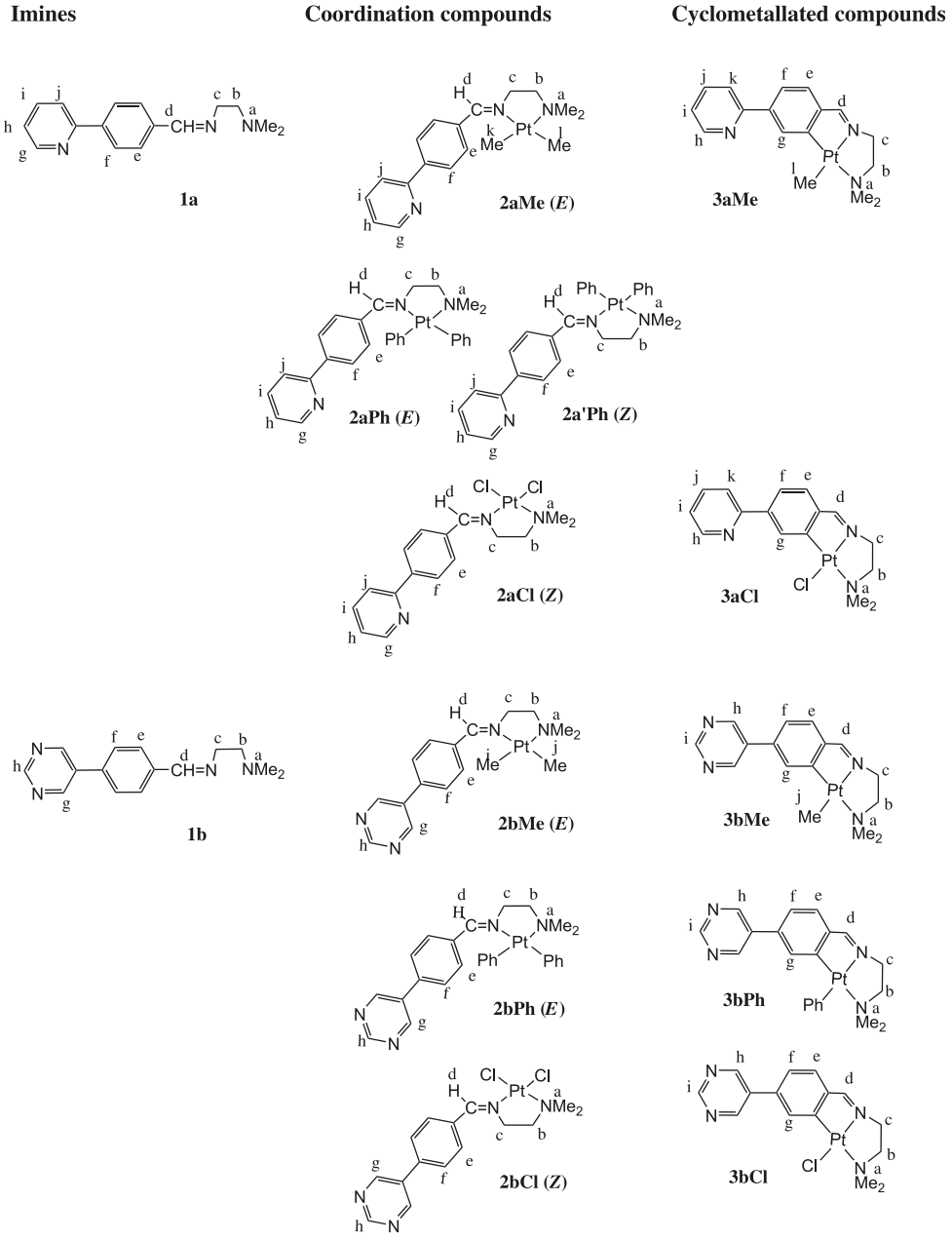
 doi:10.1139/V08-084

Chart 1.



Results and discussion

Ligands 4-(2′-C_5H_4N)$C_6H_4CHNCH_2CH_2NMe_2$ (**1a**) and 4-(3′,5′-$C_4H_3N_2$)$C_6H_4CHNCH_2CH_2NMe_2$ (**1b**) were prepared from the condensation reactions of *N,N*-dimethylethylenediamine and the corresponding aldehyde carried out in toluene at room temperature. The resulting imines were characterized by ^{1}H NMR spectroscopy.

Reactions of ligands 1a and 1b with $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$

The reactions of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ with potentially tridentate ligands **1a** and **1b** carried out in acetone at room temperature produced the compounds $[PtMe_2\{4\text{-}(2'\text{-}C_5H_4N)\text{-}C_6H_4CHNCH_2CH_2NMe_2\}]$ (**2aMe**) and $[PtMe_2\{4\text{-}(3',5'\text{-}C_4H_3N_2)C_6H_4CHNCH_2CH_2NMe_2\}]$ (**2bMe**), respectively, in which the imines act as bidentate [*N,N*′] ligands (see Chart 1).

Compound **2aMe** was characterized by elemental analyses, mass spectrometry, and ^{1}H NMR spectra. Compound **2bMe** was characterized in solution by NMR spectroscopy but it could not be isolated in a pure form, since further reaction at room temperature produces the corresponding cyclometallated compound **3bMe** within 1 h (see below). In the ^{1}H NMR spectra, two distinct resonances appear in the methyl region, both coupled with ^{195}Pt. The one at higher field with a larger coupling to ^{195}Pt is assigned to the methyl trans to the NMe_2 moiety (see Table 1). The coordination of the ligand through both nitrogen atoms is confirmed by the coupling of both amine and imine protons to platinum. The *J*(H–Pt) values for the imine proton indicate an *E* conformation of the imine as previously observed for analogous compounds (11–18).

Intramolecular activation of C–H bonds followed by

Table 1. Selected ^{1}H NMR data.

	δ(NMe_2) [^3J(H–Pt)]	CH=N [^3J(H–Pt)]	Me–Pt [^2J(H–Pt)][a]	Me–Pt [^2J(H–Pt)][b]
2aMe	2.84 (19)	9.03 (45)	0.25 (90)	0.63 (84)
2bMe	2.85 (20)	9.07 (42)	0.21 (90)	0.64 (84)
2aPh	2.67 (17)	8.84 (44)	—	—
2a′Ph	2.62 (21)	8.43 (28)	—	—
2bPh	2.67 (18)	8.87 (43)	—	—
2aCl	3.14[c]	9.58 (52)	—	—
2bCl	3.15[c]	9.57[c]	—	—
3aMe	2.86 (20)	8.64 (58)	—	1.06 (79)
3bMe	2.87 (21)	8.68 (59)	—	1.04 (78)
3bPh	2.80 (21)	8.56 (57)	—	—
3aCl	2.91 (12)	8.13 (141)	—	—
3bCl	2.93 (14)	8.43 (140)	—	—

Note: δ in ppm, J in Hz.
[a]Me trans to NMe_2.
[b]Me trans to CH=N.
[c]Coupling to ^{195}Pt was not observed.

methane elimination to yield [*C,N,N′*] cycloplatinated compounds took place at room temperature for **2bMe** and when a toluene solution of compound **2aMe** was refluxed for 2 h. Compounds **3aMe** and **3bMe** were characterized by mass spectrometry, NMR spectroscopy, and elemental analyses. In addition, **3bMe** was also characterized crystallographically. In the ^{1}H NMR spectra, the methyl ligand, the dimethylamino, and the imine groups are coupled to platinum, and the values of the coupling constants are in the usual range for analogous compounds (11–18). In agreement with previous data, the J(H–Pt) values of the imine group increase from the coordination compounds to the cyclometallated compounds (see Table 1). In addition, the aromatic proton adjacent to the metallation site is also coupled to platinum and provides evidence of the cyclometallation process.

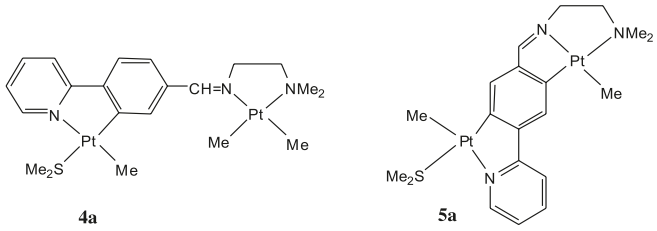
Imine **1a** derived from 4-(2-pyridyl)benzaldehyde could in principle produce binuclear compounds either mono- or doubly-cyclometallated such as **4a** and **5a** shown in Chart 2. Doubly cyclometallated compounds have been described for both platinum and palladium (21, 22). With this aim, the reaction of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ with an equimolar amount of imine **1a** was carried out in acetone.

Unfortunately, the obtained orange solid was too insoluble for NMR or mass spectra and could only be characterized by elemental analyses, which were consistent with formation of **4a**. This result indicates the ability of imine **1a** to participate in further reactions through the pyridyl nitrogen atom. Attempts to produce a doubly cyclometallated compound using longer reaction times in acetone at room temperature or refluxing a toluene suspension of compound **4a** for several hours gave insoluble materials that could not be identified. Because of the difficulties arising from the low solubility of these binuclear compounds, no further studies were carried out.

Reactions of ligands 1a and 1b with *cis*-$[PtPh_2(SMe_2)_2]$

The reactions carried out in acetone at room temperature produced compounds $[PtPh_2\{4\text{-}(2'\text{-}C_5H_4N)C_6H_4CHNCH_2CH_2NMe_2\}]$ (**2aPh**) and $[PtPh_2\{4\text{-}(3',5'\text{-}C_4H_3N_2)C_6H_4CHNCH_2CH_2NMe_2\}]$ (**2bPh**) in good yields. The obtained compounds were characterized by elemental analyses, mass spectrometry, and ^{1}H NMR spectroscopy. As for the compounds above, the coordination of the ligand through both nitrogen atoms is confirmed by the coupling of both amine and imine protons to platinum, and the J(H–Pt) values for the imine proton indicate an *E* conformation.

Chart 2.



Formation of the corresponding cyclometallated compounds was attempted by refluxing toluene solutions of **2aPh** or **2bPh** for 6 h, a method previously reported for the synthesis of analogous compounds with biphenyl ligands (18), which consists in intramolecular activation of a $C_{aromatic}$–H bond along with elimination of benzene. Using this procedure for **2bPh**, the corresponding [*C,N,N′*] cyclometallated compound $[PtPh\{4\text{-}(3',5'\text{-}C_4H_3N_2)C_6H_3CHNCH_2CH_2NMe_2\}]$ (**3bPh**) was obtained as an orange red solid. Compound **3bPh** was characterized by elemental analyses, mass spectrometry, and NMR spectra. As shown in Table 1, the coupling constant of the imine proton to platinum increases slightly compared with compound **2bPh** as a result of the formation of a metallacycle. Under the same experimental conditions, the analogous compound **3aPh** was not obtained, since red solutions were formed, and the NMR spectra taken for the final residue show only intense aldehyde signals, which indicate hydrolysis of the imine bond, along with peaks for unidentified products. Hydrolysis of imines with adventitious water in the solvent has been reported under metallation conditions with palladium or platinum substrates (23, 24). Using shorter refluxing times did not improve the results. Therefore, the synthesis of cyclometallated compound **3aPh** was attempted under milder conditions such as stirring at room temperature a solution of **2aPh** in acetone. After several hours, a new compound was formed and its spectral data, in particular a small value of J(H–Pt) for the imine proton (J(H–Pt) = 27.9 Hz), suggest isomerization of the imine from the initial *E* conformation observed in **2aPh** to the less congested *Z* form leading to compound **2a′Ph**. After 24 h, the ratio **2a′Ph/2aPh** is 0.54:1.00, and the amount of **2a′Ph** increases slowly up to a ratio of ~ 1.00:1.00 after 5 days in solution. No evidence of formation of the expected cyclometallated compound is observed in the ^{1}H NMR spectra, while small amounts of the aldehyde are formed. Isomerization from the most favoured *E* conformation of the free ligand to the *Z* conformation upon coordination to a platinum centre has been previously observed for analogous systems (18) and can be explained by the steric crowding in the coordination sphere of the platinum(II) centre, which is minimized through this conformational change. It has to be noted, however, that the adequate arrangement for producing cyclometallation at the aromatic group is the *E* conformation, since isomerization to the less

congested *Z* form places the aromatic group away from the platinum centre. Therefore, the reaction at room temperature was not a good strategy for cyclometallation of **2aPh**.

Reactions of ligands 1a and 1b with *cis*-[$PtCl_2(DMSO)_2$]

When equimolar amounts of *cis*-[$PtCl_2(DMSO)_2$] and ligand **1a** were refluxed in methanol for 5 h, the corresponding compound [$PtCl_2$\{\{4-(2′-C_5H_4N)$C_6H_4CHNCH_2CH_2NMe_2$\}] (**2aCl**) was obtained in good yield. As previously noticed for analogous systems (25), a *Z* conformation around the C=N bond is adopted with the imine proton close to the platinum nucleus, which is evidenced in the ^{1}H NMR spectrum by the downfield shift of the imine signal (δ = 9.58 ppm). This fact suggests that coordination of a bidentate ligand to a $PtCl_2$ moiety produces a conformational change from the most stable *E* conformation of the free ligand to the *Z,* and consequently *Z–E* isomerization should precede the cyclometallation step as previously reported for analogous systems. The corresponding reaction for ligand **1b** produced compound [$PtCl_2$\{4-(3′,5′-$C_4H_3N_2$)$C_6H_4CHNCH_2CH_2NMe_2$\}] (**2bCl**) as a rather insoluble impure solid; attempts to obtain **2bCl** in a pure form were unsuccessful because of its low solubility.

The most widely used conditions for converting compounds analogous to **2aCl** and **2bCl** into cycloplatinated derivatives are refluxing for several hours in either toluene or in a donor solvent such as methanol or ethanol, in some cases in the presence of an external base, which favours the formal elimination of HCl (25–30). When **2aCl** was treated with an equimolar amount of sodium acetate in refluxing methanol for 48 h, cyclometallated compound **3aCl** was produced. The process requires an initial step in which *Z* to *E* imine isomerization brings the aryl ring closer to platinum followed by the actual intramolecular C–H bond activation, which leads to a five-membered metallacycle.

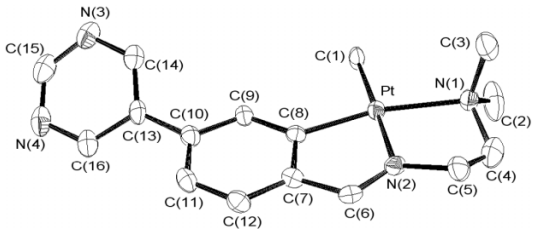
Alternatively, **3aCl** could be obtained when equimolar amounts of *cis*-[$PtCl_2(DMSO)_2$], ligand **1a** and sodium acetate were refluxed in methanol for 48 h. This method was also used to obtain **3bCl**. The obtained yields were lower than those obtained for analogous compounds derived from biphenyl such as [PtCl\{4-$C_6H_5C_6H_3CHNCH_2CH_2NMe_2$\}] and [PtCl\{2-$C_6H_5C_6H_3CHNCH_2CH_2NMe_2$\}] (18). Furthermore, using prolonged reaction times, toluene–methanol mixtures, and higher reaction temperatures (26–30) did not improve the yields, since metallic platinum and high amounts of aldehyde were formed under these conditions. Compounds **3aCl** and **3bCl** were characterized by elemental analyses, mass spectrometry, and NMR spectra. In the ^{1}H NMR spectra, a significant increase in the coupling constant of the imine proton to platinum is observed upon cyclometallation. The obtained values shown in Table 1 are in the range reported for analogous cyclometallated compounds in which a chloro ligand is in a trans position to the imine (18). As a whole, analysis of the ^{1}H NMR data reported in Table 1 indicate that the *J*(H–Pt) values for the imine proton increase in the order: **2a′Ph** (28 Hz) < **2bMe**, **2bPh**, **2aPh**, **2aMe** (42–45 Hz) < **2aCl** (52 Hz) < **3bPh**, **3aMe**, **3bMe** (57–58 Hz) << **3aCl**, **3bCl** (140–141 Hz).

This sequence is consistent with the larger *J*(H–Pt) values expected for: (*i*) cyclometallated vs. non-cyclometallated compounds, (*ii*) imine moieties trans to a chloro ligand vs. trans to a methyl or a phenyl ligand, and (*iii*) *E* vs. *Z* conformation of the imine.

Table 2. Selected bond lengths (Å) and angles (°) with estimated standard deviations for compound **3bMe**.

Bond lengths (Å)	
Pt—C(8)	1.990(5)
Pt—N(1)	2.169(4)
N(1)—C(4)	1.499(7)
N(2)—C(5)	1.457(6)
C(6)—C(7)	1.447(7)
Pt—C(1)	2.074(5)
Pt—N(2)	2.017(4)
C(4)—C(5)	1.497(8)
N(2)—C(6)	1.279(6)
C(7)—C(8)	1.436(6)
Bond angles (°)	
C(8)–Pt–N(2)	81.1(2)
N(1)–Pt–N(2)	81.9(2)
C(1)–Pt–C(8)	97.7(2)
C(1)–Pt–N(1)	99.3(2)

Fig. 1. Molecular structure of compound **3bMe**.



Crystal structure of 3bMe

Suitable crystals of **3bMe** were grown by slow diffusion of a CH_2Cl_2 solution into MeOH. The crystal structure is composed of discrete molecules separated by van der Waals interactions. Selected bond lengths and angles are given in Table 2, and a molecular view is shown in Fig. 1.[3]

The ligand behaves as [*C,N,N′*]-tridentate and a three fused [*6,5,5*] ring system containing a five-membered endo metallacycle is formed. A methyl ligand completes the square-planar coordination of the platinum atom. The metallacycle is approximately planar as suggested by the sum of internal angles, which is close to 540° (31) and nearly co-planar with both the metallated phenyl and the mean coordination plane. The dihedral angle between phenyl and pyrimidyl groups is 31.8(2)°, which suggests, aside from

[3] Supplementary data for this article are available on the journal Web site (canjchem.nrc.ca) or may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0R6, Canada. DUD 3774. For more information on obtaining material, refer to cisti-icist.nrc-cnrc.gc.ca/irm/unpub_e.shtml. CCDC 6792371 contains the crystallographic data for this manuscript. These data can be obtained, free of charge, via www.ccdc.cam.ac.uk/conts/retrieving.html (Or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).

packing effects, a compromise between van der Waals repulsion of the ortho hydrogen atoms and the co-planarity required for resonance extended to both aryl rings. Tilt angles ranging from 10.4° to 49.9° have been obtained for biphenyl systems in analogous platinum(II) and platinum(IV) cyclometallated compounds (17, 18). Bond lengths and angles are in the expected range for analogous compounds (11–13, 15–18). The Pt–NMe_2 distance is longer (2.169(4) Å) than the Pt–NCH (2.017(4) Å), which is consistent with the relatively weak coordinating ability of tertiary amines for platinum. Bond angles at platinum are close to the ideal value of 90°, and the smallest angles correspond to those involving the tridentate ligand with "bite" angles C(8)–Pt–N(2) and N(1)–Pt–N(2) being 81.1(2)° and 81.9 (2)°, respectively.

Conclusions

The results here presented indicate that [*C,N,N′*] cyclometallated compounds derived from **1a** and **1b** can be easily obtained when $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ is used as a metallation agent. The presence of two nitrogen atoms in the pyrimidyl substituent in **1b** facilitates the reaction, which takes place under milder conditions than for **1a**. When *cis*-$[PtPh_2(SMe_2)_2]$ is used as starting material, the corresponding [*C,N,N′*] cyclometallated compound could only be obtained for the more activated **1b** ligand. For both substrates $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ and *cis*-$[PtPh_2(SMe_2)_2]$, the mechanism consists of oxidative addition followed by elimination of methane (32) or benzene (33), and therefore, the presence of an additional nitrogen atom, more electronegative than a carbon atom, should have a similar activating effect in both cases.

The failure to produce cyclometallation of ligand **1a** with *cis*-$[PtPh_2(SMe_2)_2]$ is however unexpected taking into account that this metallation agent was effective for 4-biphenylimine and even for the more sterically demanding 2- biphenylimine (17, 18), and that, in this case, the presence of one nitrogen atom in **1a** should facilitate the process. Based on the observed presence of aldehyde in the attempted cyclometallation reaction, we might assume that ligand **1a** is more prone to experience hydrolysis than the corresponding biphenyl ligands. This fact along with the lower reactivity of *cis*-$[PtPh_2(SMe_2)_2]$ vs. $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (18) may account for the observed results.

When *cis*-$[PtCl_2(DMSO)_2]$ was used as starting material, the corresponding [*C,N,N′*] cyclometallated compounds could also be obtained, although with poor yields. As previously indicated for analogous systems (18, 25), the greater steric requirements of chloro vs. methyl or phenyl ligands in the platinum substrate leads to a *Z* conformation of the imine group in the [*N,N′*] compounds, and therefore, *Z* to *E* isomerization should precede the cyclometallation. Moreover, the lower yields compared with those obtained for biphenyl ligands (18) could be related to the higher proclivity of ligands **1a** and **1b** to hydrolysis as well as to the reduced reactivity towards an electrophilic reagent expected for ligands containing electron-withdrawing substituents.

As a whole, the above results indicate that pyridyl or pyrimidyl substituents on the aryl group may have a decisive influence in the cyclometallation process, which is attributed more to electronic than to steric effects, since the substituents are away from the metallation position. In addition to determining the success and ease of the cyclometallation, these substituents emphasize the differences observed when different metallating agents such as $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$, *cis*-$[PtPh_2(SMe_2)_2]$, and *cis*-$[PtCl_2(DMSO)_2]$ are used, which is further evidence of the different mechanisms operating for such substrates (19). Further work aimed at evaluating the ability of free pyridyl or pyrimidyl groups in the new compounds to coordinate a second metallic fragment is in progress.

Experimental

General

NMR spectra were performed at the Unitat de RMN d'Alt Camp de la Universitat de Barcelona using Mercury 400 and Varian 300 spectrometers and referenced to $SiMe_4$. δ values are given in ppm and *J* values in Hz. *J*(H–Pt) values were measured at 300 MHz to avoid errors arising from broadening of the ^{195}Pt satellites observed at 400 MHz. Labelling of the compounds is as shown in Chart 1. ES-mass spectra were performed at the Servei d'Espectrometria de Masses de la Universitat de Barcelona using a VG-Quattro spectrometer. Microanalyses were performed by the Servei de Recursos Científics i Tècnics de la Universitat Rovira i Virgili (Tarragona).

All starting materials were purchased from commercial sources and used as received. Toluene was distilled from sodium–benzophenone. Compounds $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (34), *cis*-$[PtPh_2(SMe_2)_2]$ (35, 36), and *cis*-$[PtCl_2(DMSO)_2]$ (37) were prepared according to literature methods.

Preparation of the compounds

Compounds **1** were prepared by the reaction of equimolar amounts of *N*,*N*-dimethylethylenediamine and the corresponding aldehyde in toluene (20 mL). The mixture was stirred for 1 h and dried over Na_2SO_4. The solvent was removed in a rotary evaporator to yield yellow oils.

4-(2′-C_5H_4N)$C_6H_4CHNCH_2CH_2NMe_2$ (1a)

Obtained from 0.5 g (2.90×10^{-3} mol) of 4-(2-pyridyl)benzaldehyde and 0.26 g of *N*,*N*-dimethylethylenediamine. Yield: 0.5 g (67%). ^1H NMR (400 MHz, $CDCl_3$) δ: 2.32 [s, 6H, H^a], 2.67 [t, *J*(H–H) = 7.2, 2H, H^b], 3.78 [td, *J*(H–H) = 7.2, 0.8, 2H, H^c], 7.26 [m, 1H, H^h], 7.77 [m, 2H, $H^{i,j}$], 7.84 [d, *J*(H–H) = 8.4, 2H, H^f], 8.05 [d, *J*(H–H) = 8.4, 2H, H^e], 8.37 [s, 1H, H^d], 8.71 [dt, *J*(H–H) = 4.4, 1.4, 1H, H^g].

4-(3′,5′-$C_4H_3N_2$)$C_6H_4CHNCH_2CH_2NMe_2$ (1b)

Obtained from 0.4 g of 5-(4-formylphenyl)pyrimidine (2.17×10^{-3} mol) and 0.19 g of *N*,*N*-dimethylethylenediamine. Yield: 0.4 g (72%). ^1H NMR (400 MHz, $CDCl_3$) δ: 2.34 [s, 6H, H^a], 2.69 [t, *J*(H–H) = 7.2, 2H, H^b], 3.80 [t, *J*(H–H) = 7.2, 2H, H^c], {7.64 [d, *J*(H–H) = 8.4, 2H], 7.89 [d, *J*(H–H) = 8.4, 2H], $H^{e,f}$}, 8.38 [s, 1H, H^d], 8.98 [s, 2H, H^g], 9.23 [s, 1H, H^h].

[PtMe$_2${4-(2′-C$_5$H$_4$N)C$_6$H$_4$CHNCH$_2$CH$_2$NMe$_2$}] (2aMe)

Compound **2aMe** was obtained from 88 mg (3.49×10^{-4} mol) of ligand **1a** and 100 mg (1.74×10^{-4} mol) of compound [Pt$_2$Me$_4$(μ-SMe$_2$)$_2$] in acetone (20 mL). The mixture was stirred for 30 min at room temperature. **2aMe** was obtained as an orange solid upon removal of the acetone in a rotary evaporator and washing of the residue with ether (3×2 mL).

Yield: 150 mg (90%). ^{1}H NMR (400 MHz, CDCl$_3$) δ: 0.25 [s, ^2J(Pt–H) = 90, 3H, H^k], 0.63 [s, ^2J(Pt–H) = 84, 3H, H^l], 2.71 [t, J(H–H) = 5.2, 2H, H^b], 2.84 [s, ^3J(H–Pt) = 19, 6H, H^a], 4.07 [t, J(H–H) = 5.2, 2H, H^c], 7.76–7.79 [m, 3H, H^{h,i,j}], {8.01 [d, J(H–H) = 8.2, 2H], 8.37 [d, J(H–H) = 8.2, 2H],H^{e,f}}, 8.70 [d, J(H–H) = 5.2, 1H, H^g], 9.03 [s, ^3J(Pt–H) = 45, 1H, H^d]. ES (+)-MS (MeCN – H$_2$O): 504 [M – Me + MeCN], 489 [M – 2Me + MeCN], 463 [M – Me], 448 [M – 2Me]. Anal. found: C, 44.5; H, 5.9; N, 8.5. Calcd. for C$_{18}$H$_{25}$N$_3$Pt: C, 45.18; H, 5.26; N, 8.78 (%).

[PtMe$_2${4-(3′,5′-C$_4$H$_3$N$_2$)C$_6$H$_4$CHNCH$_2$CH$_2$NMe$_2$}] (2bMe)

Compound **2bMe** was obtained following the same procedure from 18 mg of ligand **1b** and 20 mg (0.35×10^{-4} mol) of compound [Pt$_2$Me$_4$(μ-SMe$_2$)$_2$] in acetone (10 mL). Compound **2bMe** could be characterized in solution, and within an hour, produces **3bMe** (see below).

^{1}H NMR (400 MHz, CDCl$_3$) δ: 0.21 [s, ^2J(Pt–H) = 90, 3H, H^i], 0.64 [s, ^2J(Pt–H) = 84, 3H, H^j], 2.72 [m, 2H, H^b], 2.85 [s, ^3J(H–Pt) = 20, 6H, H^a], 4.11 [m, 2H, H^c], {7.60 [d, J(H–H) = 8.4, 2H], 8.45 [d, J(H–H) = 8.4, 2H], H^{e,f}}, 9.00 [s, 2H, H^g], 9.07 [s, ^3J(Pt–H) = 42, 1H, H^d], 9.24 [s, 1H, H^h].

[PtPh$_2${4-(2′-C$_5$H$_4$N)C$_6$H$_4$CHNCH$_2$CH$_2$NMe$_2$}] (2aPh)

Compound **2aPh** was obtained as a yellow solid following the same procedure as for **2aMe** from 48 mg (0.19 mmol) of ligand **1a** and the equimolar amount of compound *cis*-[PtPh$_2$(SMe$_2$)$_2$] (90 mg) in acetone (10 mL).

Yield: 80 mg (70%). ^{1}H NMR (400 MHz, CDCl$_3$) δ: 2.67 [s, ^3J(Pt–H) = 17, 6H, Me^a], 2.79 [t, J(H–H) = 5.0, 2H, H^b], 4.21 [t, J(H–H) = 5.0, 2H, H^c], {6.28 [t, J(H–H) = 7.0, 1H], 6.38 [t, J(H–H) = 7.4, 2H], 6.81 [t, J(H–H) = 7.2, 1H], 6.93 [m, 4H], 7.23 [ddd, J(H–H) = 7.6, 4.8, 1.2, 1H], 7.48 [d, J(H–H) = 8.0, 2H], 7.55–7.58 [m, 3H], 7.73 [td, J(H–H) = 7.6, 2, 1H], 8.14 [d, J(H–H) = 8.4, 2H], 8.65 [ddd, J(H–H) = 4.4, 1.6, 1.0, 1H]}, 8.84 [s, ^3J(Pt–H) = 44, 1H, H^d]. ES (+)-MS (MeCN – H$_2$O): 603 [M + H], 525 [M – Ph], 448 [M – 2Ph]. Anal. found: C, 54.5; H, 4.9; N, 6.5. Calcd. for C$_{28}$H$_{29}$N$_3$Pt·H$_2$O: C, 54.18; H, 5.03; N, 6.77 (%). Isomerization to **2a′Ph** (*Z* isomer) took place in acetone at room temperature. ^{1}H NMR (400 MHz, CDCl$_3$) δ: 2.62 [s, ^2J(Pt–H) = 21, 6H, Me^a], 2.76 [t, J(H–H) = 6.0, 2H, H^b], 4.02 [td, J(H–H) = 6.0, 2,0, 2H, H^c], 8.43 [s, ^3J(Pt–H) = 28, 1H, H^d].

[PtPh$_2${4-(3′,5′-C$_4$H$_3$N$_2$)C$_6$H$_4$CHNCH$_2$CH$_2$NMe$_2$}] (2bPh)

Compound **2bPh** was obtained as a yellow solid following the same procedure as for **2aMe** from 48.3 mg (0.19 mmol) of ligand **1b** and the equimolar amount of compound *cis*-[PtPh$_2$(SMe$_2$)$_2$] (90 mg) in acetone (10 mL).

Yield: 90 mg (78%). ^{1}H NMR (400 MHz, CDCl$_3$) δ: 2.67 [s, ^3J(Pt–H) = 18, 6H, Me^a], 2.80 [t, J(H–H) = 5.0, 2H, H^b], 4.20 [t, J(H–H) = 5.0, 2H, H^c], {6.34–6.36 [m, 2H], 6.80 [t, J(H–H) = 8.0, 2H], 6.89–6.92 [m, 3H], 7.12 [d, J(H–H) = 8.4, 2H], 7.44–7.46 [m, 3H], 8.12 [d, J(H–H) = 8.0, 2H], 8.81 [s, 2H], 9.20 [s, 1H], aromatics}, 8.87 [s, ^3J(Pt–H) = 43, 1H, H^d]. ES (+)-MS (MeCN – H$_2$O): 604 [M + H], 526 [M – Ph], 449 [M – 2Ph]. Anal. found: C, 53.2; H, 4.8; N, 9.0. Calcd. for C$_{27}$H$_{28}$N$_4$Pt: C, 53.72; H, 4.67; N, 9.28 (%).

[PtCl$_2${4-(2′-C$_5$H$_4$N)C$_6$H$_4$CHNCH$_2$CH$_2$NMe$_2$}] (2aCl)

Compound **2aCl** was obtained from 150 mg (3.50×10^{-4} mol) of *cis*-[PtCl$_2$(DMSO)$_2$] and the equimolar amount (90.0 mg) of **1a** after refluxing the mixture in methanol for 5 h. On cooling, a light yellow solid is formed.

Yield: 120 mg (65%). ^{1}H NMR (400 MHz, CDCl$_3$) δ: 2.70 [t, ^2J(H–H) = 6.0, 2H, H^b], 3.14 [s, 6H, Me^a], 4.09 [td, ^2J(H–H) = 6.0, 2.0, 2H, H^c], 7.33 [ddd, J(H–H) = 6.8, 4.8, 2, 1H, H^h], 7.64 [d, ^3J(H–H) = 8.4, 2H, H^e or H^f], 7.80–7.82 [m, 2H, H^i, H^j], 8.13 [d, ^3J(H–H) = 8.4, 2H, H^e or H^f], 8.73 [dt, J(H–H) = 4.8, 2, 1H, H^g], 9.58 [s, ^3J(Pt–H) = 52, 1H, H^d]. ESI-MS: 520 [M + H], 484 [M – Cl]. Anal. found: C, 36.2; H, 3.7; N, 8.0. Calcd. for C$_{16}$H$_{19}$Cl$_2$N$_3$Pt·H$_2$O: C, 35.76; H, 3.94; N, 7.82 (%).

[PtCl$_2${4-(3′,5′-C$_4$H$_3$N)C$_6$H$_4$CHNCH$_2$CH$_2$NMe$_2$}] (2bCl)

Compound **2bCl** was obtained as an insoluble impure solid following the procedure reported above for **2aCl**.

^{1}H NMR (400 MHz, CDCl$_3$) δ: 2.72 [m, 2H, H^b], 3.15 [s, 6H, Me^a], 4.08 [t ^2J(H–H) = 6.0, 2H, H^c], 7.73–7.76 [m, 4H], 8.99 [s, 2H,], 9.29 [s, 1H], 9.57 [s, 1H, H^d].

[PtMe{4-(2′-C$_5$H$_4$N)C$_6$H$_3$CHNCH$_2$CH$_2$NMe$_2$}] (3aMe)

Compound **3aMe** was obtained after refluxing a toluene solution (20 mL) containing 50 mg of compound **2aMe** for 2 h. Toluene was totally removed, and the residue was recrystallized from CH$_2$Cl$_2$–MeOH to yield **3aMe** as a red solid.

Yield: 40 mg (83%). ^{1}H NMR (400 MHz, CDCl$_3$) δ: 1.06 [s, ^2J(Pt–H) = 79, 3H, H^l], 2.86 [s, ^3J(H–Pt) = 20, 6H, H^a], 3.19 [t, J(H–H) = 5.2, 2H, H^b], 4.09 [t, J(H–H) = 5.2, 2H, H^c], 7.19 [m, 2H, H^{i,j}], {7.37 [d, J(H–H) = 8.0, 2H], 7.82 [d, J(H–H) = 8.0, 2H],H^{e,f}}, 7.73 [d, J(H–H) = 6.8, 1H, H^k], 8.07 [d, J(H–H) = 2, ^3J(Pt–H) = 67, 1H, H^g], 8.64 [s, ^3J(H–Pt) = 58, 1H, H^d], 8.67 [d, J(H–H) = 4.8, 1H, H^h]. ES (+)-MS (MeCN – H$_2$O): 488 [M – Me + MeCN], 462 [M]. Anal. found: C, 44.0; H, 4.7; N, 8.5. Calcd. for C$_{17}$H$_{21}$N$_3$Pt: C, 44.15; H, 4.58; N, 9.09 (%).

[PtMe{4-(3′,5′-C$_4$H$_3$N$_2$)C$_6$H$_3$CHNCH$_2$CH$_2$NMe$_2$}] (3bMe)

Compound **3bMe** was obtained from 89 mg (3.49×10^{-4} mol) of ligand **1b** and 100 mg (1.74×10^{-4} mol) of compound [Pt$_2$Me$_4$(μ-SMe$_2$)$_2$] in acetone (20 mL). The mixture was stirred for 1 h at room temperature, metallic platinum was filtered off, and acetone was removed in a rotary evaporator. Red crystals of **3bMe** were obtained upon recrystallization of the residue from CH$_2$Cl$_2$–MeOH.

Yield: 100 mg (62%). ^{1}H NMR (400 MHz, CDCl$_3$) δ: 1.04 [s, ^2J(Pt–H) = 78, 3H, H^j], 2.87 [s, ^3J(H–Pt) = 21, 6H, H^a], 3.21 [t, J(H–H) = 6.0, 2H, H^b], 4.12 [td, J(H–H) = 6.0, 1.2, 2H, H^c], 7.16 [dd, J(H–H) = 7.6, 1.6, 1H, H^f], 7.38 [d, J(H–H) = 7.6, ^4J(H–Pt) = 10, 1H, H^e], 7.82 [d, J(H–H) = 2.0, ^3J(H–Pt) = 65, 1H, H^g], 8.68 [s, ^3J(H–Pt) = 59, 1H, H^d],

8.97 [s, 2H, H^h], 9.17 [s, 1H, H^i]. ES (+)-MS (MeCN – H_2O): 489 [M – Me + MeCN], 463 [M], 448 [M – Me]. Anal. found: C, 41.0; H, 4.3 N, 11.7. Calcd. for $C_{16}H_{20}N_4Pt$: C, 41.47; H, 4.35; N, 12.09 (%).

[PtPh{4-(3′,5′-$C_4H_3N_2$)C_6H_3CHNCH$_2$CH$_2$NMe$_2$}] (3bPh)

Compound **3bPh** was obtained from 50 mg (8.3×10^{-5} mol) of **2bPh** in 20 mL of toluene. The mixture was refluxed for 6 h, and toluene was removed in a rotary evaporator. The residue was washed with ether to yield an orange–red solid.

Yield: 33 mg (76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.80 [s, ^3J(H–Pt) = 21, 6H, H^a], 3.24 [t, J(H–H) = 6.0, 2H, H^b], 4.11 [td, J(H–H) = 6.0, 1.2, 2H, H^c], 6.95 [tt, J(H–H) = 7.4, 1.6, 1H, *p*-Ph], 7.10 [t, J(H–H) = 7.4, 2H, *m*-Ph], 7.15 [dd, J(H–H) = 7.4, 1.6, 1H, H^g], 7.32 [d, J(H–H) = 1.6, 1H, H^e], 7.37 [d, J(H–H) = 8, 1H, H^f], 7.55 [dd, J(H–H) = 8, 1.6, ^3J(H–Pt) = 59, 2H, *o*-Ph], 8.56 [s, ^3J(H–Pt) = 57, 1H, H^d], 8.79 [s, 2H, H^h], 9.10 [s, 1H, H^i]. ES (+)-MS (MeCN – H_2O): 973 [2M – Ph], 526 [M]. Anal. found: C, 48.7; H, 4.2; N, 10.2. Calcd. for $C_{21}H_{22}N_4Pt$: C, 48.00; H, 4.22; N, 10.66 (%).

[PtCl{4-(2′-C_5H_4N)C_6H_3CHNCH$_2$CH$_2$NMe$_2$}] (3aCl)

Compound **3aCl** was prepared from 50 mg (9.6×10^{-5} mol) of **2aCl** and the equimolar amount of $Na(CH_3COO)$ (8 mg) after refluxing the mixture in methanol for 48 h. The reaction mixture was cooled, filtered to remove unreacted materials, and concentrated to dryness. The obtained residue was recrystallized in dichloromethane–methanol to yield an orange solid.

Yield: 15 mg (32%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.91 [s, ^3J(H–Pt) = 12, 6H, H^a], 3.11 [t, ^2J(H–H) = 6.0, 2H, H^b], 3.97 [t, ^2J(H–H) = 6.0, 2H, H^c], 7.22 [ddd, J(H–H) = 7.6, 5.0, 1.2, 1H, H^i], 7.32 [d, ^3J(H–H) = 8.0, 1H, H^k], 7.74 [td, J(H–H) = 7.6, 1.6, 1H, H^j], 7.79 [dd, J(H–H) = 8, 1.6, 1H, H^e], 7.87 [d, ^3J(H–H) = 8.0, 1H, H^f], 8.13 [s, ^3J(Pt–H) = 141, 1H, H^d], 8.18 [d, ^4J(H–H) = 1.6, 1H, H^g], 8.67 [dd, J(H–H) = 5.0, 1.6, 1H, H^h]. ES (+)-MS (MeCN – H_2O): 447 [M – Cl]. Anal. found: C, 37.6; H, 4.1; N, 8.5. Calcd. for $C_{16}H_{18}ClN_3Pt{\cdot}H_2O$: C, 38.36; H, 4.02; N, 8.39 (%).

[PtCl{4-(3′,5′-$C_4H_3N_2$)C_6H_3CHNCH$_2$CH$_2$NMe$_2$}] (3bCl)

Compound **3bCl** was prepared from 100 mg (2.37×10^{-4} mol) of *cis*-[$PtCl_2(DMSO)_2$], 60.2 mg of **1b**, and 20 mg of sodium acetate after refluxing the mixture in methanol for 48 h. The reaction mixture was cooled, filtered to remove unreacted materials, and concentrated to dryness. The obtained residue was recrystallized in dichloromethane–pentane to yield an orange solid.

Yield: 20 mg (17.4%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.93 [s, ^3J(H–Pt) = 14, 6H, H^a], 3.15 [t, ^2J(H–H) = 6.0, 2H, H^b], 4.15 [td, ^2J(H–H) = 6.0, 1.2, ^3J(H–Pt) = 34, 2H, H^c], 7.21 [dd, J(H–H) = 8.0, 2.0, 1H, H^e], 7.39 [d, ^3J(H–H) = 8.0, 1H, H^f], 7.98 [d, J(H–H) = 2.0, 1H, H^g], 8.43 [t, J(H–H) = 1.2, ^3J(Pt–H) = 140, 1H, H^d], 9.02 [s, 2H, H^h], 9.19 [s, 1H, H^i]. ES (+)-MS (MeCN – H_2O): 503 [M + H_2O]. Anal. found: C, 33.3; H, 3.5; N, 9.5. Calcd. for $C_{15}H_{17}ClN_4Pt{\cdot}CH_2Cl_2$: C, 33.78; H, 3.37; N, 9.85 (%).

Table 3. Crystallographic and refinement data for compound **3bMe**.

Formula	$C_{16}H_{20}N_4Pt$
FW	463.45
T (K)	125(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	11.0787(8)
b (Å)	16.981(1)
c (Å)	8.1766(6)
β (°)	94.310(1)
V (Å^3)	1533.9(2)
Z	4
$D_{calcd.}$ (g/cm^3)	2.007
Abs. coeff. (mm^{-1})	9.146
θ range (°)	1.84–28.28
% Completeness to θ max	99.4
Data collected, unique	19507, 3781 (R_{int} = 0.0561)
Data, restraints, parameters	3781, 0, 193
GOF on F^2	1.023
R_1, wR_2 (F^2, $I > 2\sigma(I)$)	0.0295, 0.0574
R_1, wR_2 (F^2, all data)	0.0465, 0.0624
Peak and hole, e/Å^{-3}	1.522 and –0.792

4a

Compound **4a** was prepared from 22 mg (8.7×10^{-5} mol) of ligand **1a** and 50 mg (8.7×10^{-5} mol) of compound [$Pt_2Me_4(\mu\text{-}SMe_2)_2$] in acetone (20 mL). The mixture was stirred for 5 h at room temperature, and the resulting orange solid was filtered.

Yield: 60 mg (92%). **4a** was too insoluble for NMR or mass spectra. Anal. found: C, 33.3; H, 4.9 N, 5.2. Calcd. for $C_{21}H_{34}N_3Pt_2S$: C, 33.60; H, 4.56; N, 5.60 (%).

5a

The preparation of compound **5a** was attempted using a procedure consisting of refluxing a toluene suspension of compound **4a** for 2 h. The obtained solid was too insoluble for NMR or mass spectra, and the elemental analysis was not consistent with the expected formula. An alternative procedure detailed below gave analogous results: 25 mg (5.2×10^{-5} mol) of compound **3a** and 15 mg (2.6×10^{-5} mol) of compound [$Pt_2Me_4(\mu\text{-}SMe_2)_2$] were allowed to react in acetone at room temperature for 16 h. The resulting insoluble solid was filtered. Yield: 30 mg (79%, based on the expected formula $C_{20}H_{30}N_3Pt_2S$).

X-ray structure determination

X-ray diffraction data were collected on a Bruker APEX 2 CCD platform diffractometer (Mo Kα, λ = 0.71073 Å) at 125 K (0 °C = 273.15 K). A suitable crystal was mounted in a nylon loop with Paratone–*N* cryoprotectant oil. During data examination and space-group determination with XPREP, the σ(I) values were normalized and multiplied by a factor of 0.5. The structure was solved using direct methods and standard difference map techniques, and was refined by full-matrix least-squares procedures on F^2 with SHELXTL (Version 6.14) (38). All non-hydrogen atoms were refined

anisotropically. Hydrogen atoms were included in calculated positions and were refined using a riding model. Crystal data and refinement details are presented in Table 3.

Acknowledgements

We thank the Ministerio de Ciencia y Tecnología (project: CTQ2006-02007/BQU (MC)), Bard College, Vassar College, and The National Science Foundation (Grant NSF 0521237 to JMT (PI) and CMA) for financial support.

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