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Steric and electronic effects on the regioselective formation of platinum(II) metallacycles: crystal structure of [PtMe(3-MeC$_6$H$_3$CH=NCH$_2$C$_6$H$_5$)(PPh$_3$)]

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Abstract

The reaction of [Pt$_2$Me$_4$(μ-SMe$_2$)$_2$] (1) with imines 3,4-(OMe)$_2$C$_6$H$_3$CH=NCH$_2$Ph (2c) and 3-MeC$_6$H$_4$CH=NCH$_2$Ph (2e) yields cyclometallated compounds [PtMe(3,4-(OMe)$_2$C$_6$H$_2$CH=NCH$_2$Ph)(SMe$_2$)] (4c) and [PtMe(3-MeC$_6$H$_3$CH=NCH$_2$Ph)(SMe$_2$)] (4e) arising from selective metallation at the less hindered of the two non-equivalent *ortho* positions of the aryl ring, followed by loss of methane. These compounds react with PPh$_3$ to give cyclometallated compounds [PtMe(3,4-(OMe)$_2$C$_6$H$_2$CH=NCH$_2$Ph)(PPh$_3$)] (5c) and [PtMe(3-MeC$_6$H$_3$CH=NCH$_2$Ph)(PPh$_3$)] (5e). Imines 2,4,6-(OMe)$_3$C$_6$H$_2$CH=NCH$_2$Ph (2a), 3,5-(OMe)$_2$C$_6$H$_3$CH=NCH$_2$Ph (2b) and 2,5-Me$_2$C$_6$H$_3$CH=NCH$_2$Ph (2d) coordinate to platinum through the nitrogen atom to yield compounds [PtMe$_2$(ArCH=NCH$_2$Ph)(SMe$_2$)] (3) but fail to produce cyclometallated compounds.

Keywords: Platinum; Cyclometallation; Platinocycles; Imine

1. Introduction

The rapid growth of the chemistry of cyclometallated complexes is due to their successful application in organic synthesis, catalysis, asymmetric synthesis and photochemistry. Cyclopalladation reactions of N-donor ligands have been studied extensively [1] and, in general, the mechanism consists of an intramolecular electrophilic attack of the palladium at the carbon atom. On the other hand, platinum(II) can display either electrophilic or nucleophilic features in intramolecular metallation [2]. If activation of several C–H bonds is possible, the regioselectivity of the process is mainly determined by the operating mechanism since for an electrophilic metal the highest electron density carbon will be favoured while for a nucleophilic metal the reaction will take place at the most electron-deficient carbon. Steric effects of bulky groups may also regulate the regioselectivity since it has been shown that the presence of non-coordinating substituents in the carbon atom adjacent to the metallation position hinders the cyclometallation reaction [3]. The preference for a metallation site with a lower steric hindrance has also been reported in the formation of cyclomanganated derivatives [4].

We have recently reported the formation of cyclometallated platinum(II) compounds with fluorinated iminic ligands and, in this system, metallation occurs in spite of the presence of fluorine substituents adjacent to the activated C–H bond, as for ligand 3,5-F$_2$C$_6$H$_3$CH=NCH$_2$Ph. Moreover, for asymmetric ligand 3-FC$_6$H$_4$CH=NCH$_2$Ph, metallation takes place exclusively at the position adjacent to the fluorine atom [5]. The activating effect of the fluorine atom may be attributed to its electron-withdrawing ability since, in this system, the platinum substrate acts as a nucleophile [6]. In order to have a better understanding of the stereo-electronic effects of the substituents involved in the regioselectivity of the C–H bond activation, we extended our studies to analogous reactions with substituted iminic ligands. *N*-benzylidenebenzylamines, bearing methoxy or methyl groups adjacent to the metallation position in the benzal ring, were selected for this study. Different results from those reported for such

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imines in cyclopalladation reactions could be anticipated since the palladium substrate acts as an electrophile.

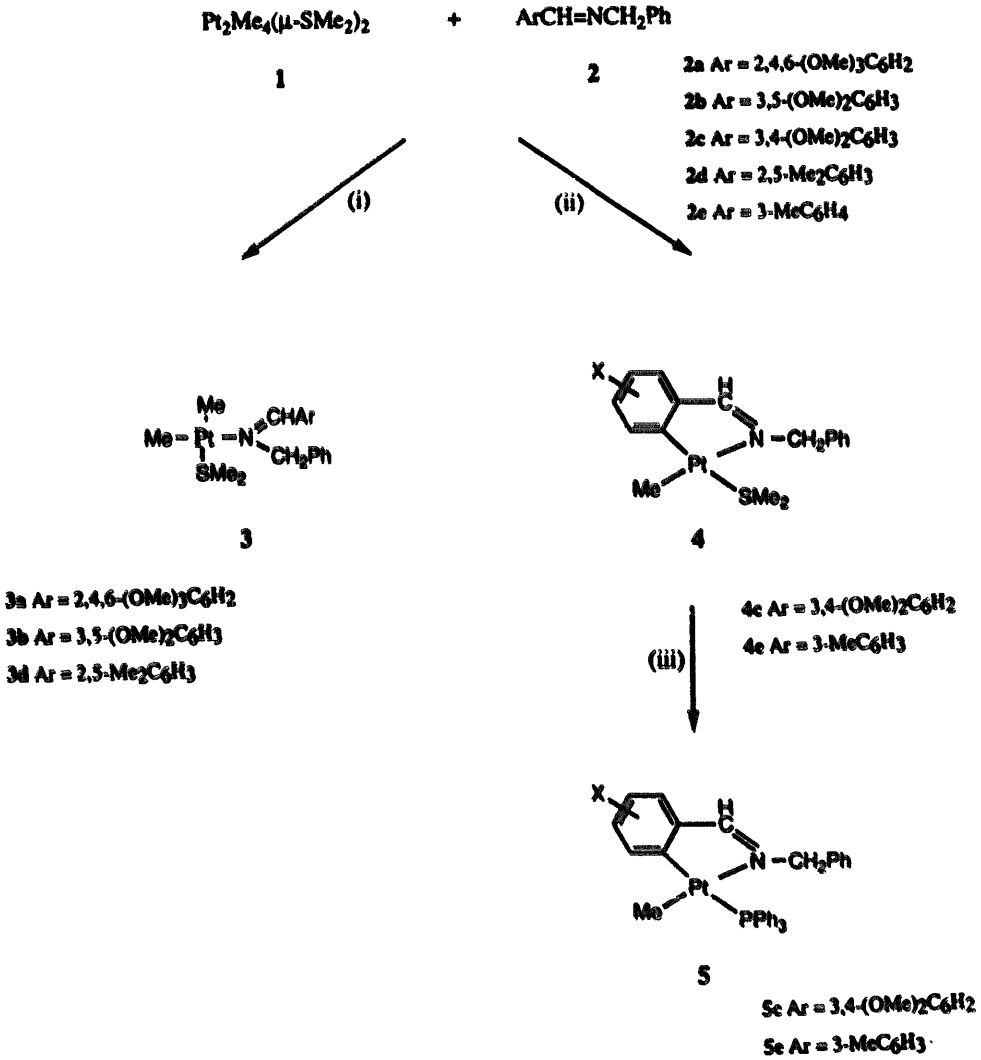
We have reported elsewhere that platinum(IV) cyclometallated compounds containing *N*-benzylidenebenzylamines can be obtained by intramolecular oxidative addition of C(aryl)–X bonds (X = F, Cl or Br) to the platinum substrate [5–8]. Analogous reactions for azine phosphines have been recently reported [9]. With the aim of achieving activation of C–O bonds in a similar process, the reaction with 2,4,6-$(OMe)_3C_6H_2$-$CH{=}NCH_2Ph$ was also studied.

2. Results and discussion

The reactions of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (**1**) with iminic ligands $ArCH{=}NCH_2Ph$ containing methoxy or methyl groups (**2a–2e**) were carried out in acetone and the results are shown in Scheme 1. Formation of cyclometallated compounds $[PtMe\{3,4\text{-}(OMe)_2C_6H_2CH{=}NCH_2Ph\}(SMe_2)]$ (**4c**) and $[PtMe(3\text{-}MeC_6H_3CH{=}NCH_2Ph)(SMe_2)]$ (**4e**) by *ortho* metallation with loss of methane was achieved only for imines 3,4-$(OMe)_2C_6H_3CH{=}NCH_2Ph$ (**2c**) and 3-$MeC_6H_4CH{=}NCH_2Ph$ (**2e**).

Coordination of the imine ligand to platinum through the nitrogen atom yielding compounds $[PtMe_2(Ar\text{-}CH{=}NCH_2Ph)(SMe_2)]$ (**3**) has been postulated as a previous step to the intramolecular C(aryl)–H activation process [7,8]. However, when the reactions of imines **2c** and **2e** with $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (**1**) were monitored by ^1H NMR, such compounds were not detected, indicating that the subsequent cyclometallation process is fast on the NMR time scale.

In contrast, the reaction of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (**1**)



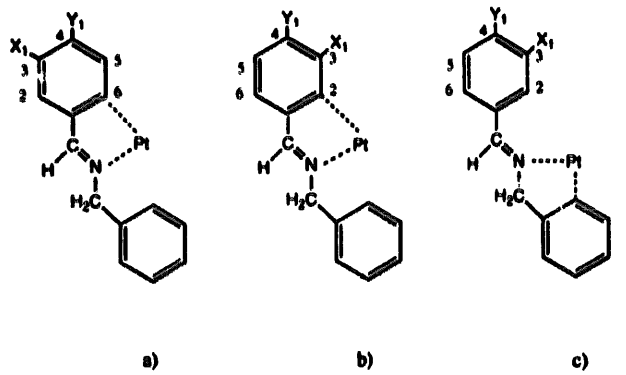
Scheme 1. (i) Acetone, room temperature, 30 min; (ii) $-CH_4$, acetone room temperature, 16 h; (iii) $+PPh_3$ (1 : 1), acetone, room temperature, 16 h.

with the imines 2,4,6-$(OMe)_3C_6H_2CH{=}NCH_2Ph$ (**2a**), 3,5-$(OMe)_2C_6H_3CH{=}NCH_2Ph$ (**2b**) and 2,5-$Me_2C_6H_3CH{=}NCH_2Ph$ (**2d**) yielded $[PtMe_2(ArCH{=}NCH_2Ph)(SMe_2)]$ (**3**). No further reaction to yield cyclometallated compounds was observed in acetone solution at room temperature, and more drastic conditions led to decomposition yielding metallic platinum and free imine.

Compounds **3** could not be isolated in a pure form and they were characterized by ^1H NMR in solution. The two methyl–platinum resonances appear as singlets with platinum satellites ($^2J(HPt) \approx 80$–86 Hz). The coordination of the imine to platinum was confirmed by the coupling of the iminic proton with platinum ($^3J(HPt) \approx 45$–51 Hz).

For the compound $[PtMe_2\{2,4,6\text{-}(OMe)_3C_6H_2CH{=}NCH_2Ph\}(SMe_2)]$ (**3a**), activation of the C–O bond, as reported for compounds $[PtX_2(R_2PC_6H_4R')_2]$ [10], was not achieved. For the compound $[PtMe_2\{3,5\text{-}(OMe)_2C_6H_3CH{=}NCH_2Ph\}(SMe_2)]$ (**3b**), the failure to activate the C–H bonds at the *ortho* positions is likely to result from the steric hindrance of the adjacent methoxy groups. For the compound $[PtMe_2(2,5\text{-}Me_2C_6H_3CH{=}NCH_2Ph)(SMe_2)]$ (**3d**), one of the *ortho* positions is blocked by a methyl group, while at the other the adjacent methyl group inhibits the activation of the C–H bond. Analogous ligands to **2a**, **2b** and **2d** have been reported to yield, upon reaction with $Pd(AcO)_2$, six-membered palladocycles arising from activation of C–O bonds [11] or C(aliphatic)–H bonds [12]. The different behaviour may be related to the different mechanism operating for the palladium and the platinum substrates.

As mentioned above, cyclometallated compounds $[PtMe(RCH{=}NCH_2Ph)(SMe_2)]$ R = $3,4\text{-}(OMe)_2C_6H_2$ (**4c**) and $3\text{-}MeC_6H_3$ (**4e**) were obtained. Two different platinum(II) metallacycles, either with an *endo*-cyclic or with an *exo*-cyclic structure (containing or not containing respectively the C=N group) could theoretically have been formed (Fig. 1). However, the formation of the latter can be ruled out since we have previously



a) b) c)

Fig. 1. Possible structures of platinacycles: (a) *endo* (metallation at C_6); (b) *endo* (metallation at C_2); (c) *exo*.

shown that the formation of *exo*-platinacycles by C–H bond activation is not favoured [8]. As shown in Fig. 1, for imines **2c** and **2e**, two distinct *endo*-metallacycles may be obtained since the two *ortho* positions of the benzal ring (C_2 and C_6) are not equivalent. In both reactions, only one compound was formed, indicating that metallation occurred regioselectively at one of the positions. Since no C–H bond activation took place when methoxy or methyl groups occupied positions adjacent to the metallation sites, as observed for ligands **2b** and **2d**, it is more likely that the metallation site for ligands **2c** and **2e** is the less-hindered C_6.

The reactions of **4c** and **4e** with triphenylphosphine in acetone yielded cyclometallated compounds $[PtMe(RCH{=}NCH_2Ph)(PPh_3)]$ (**5**). Even when the reaction was carried out using an excess of phosphine, the Pt–N bond was not cleaved and, consequently, the platinacycle did not open up. We have reported previously that the presence of a substituent such as a fluorine atom adjacent to the platinum facilitates the metallacycle cleavage upon reaction with triphenylphosphine [13]; this result may arise from the steric repulsion between the methyl group bound to platinum and fluorine F_5 in the corresponding compound **4**. According to the results obtained, we suggest that, for **4c** and **4e**, the metallated carbon should be C_6, with no adjacent methyl or methoxy groups.

Compounds **4c**, **4e**, **5c** and **5e**, were characterized by elemental analysis and ^1H NMR spectra, together with ^{31}P NMR spectra for the phosphine derivatives. In the ^1H NMR spectra the resonance for the methyl–platinum group appears as a singlet for **4** and as a doublet, owing to coupling with the phosphorus atom, for **5**. In both cases, the methyl group is coupled to platinum ($^2J(HPt) \approx 83$–84 Hz). The iminic and the benzylic protons are coupled to platinum, thus indicating that the imine is bound to platinum in a bidentate (CN) fashion. No coupling between the imine proton and the phosphorus atom is observed, and this is consistent with a mutual *cis* arrangement of the phosphorus and nitrogen atoms. In the ^{31}P NMR spectra, a single resonance appears and the value of $^1J(PPt)$ is consistent with the presence of an aryl carbon atom *trans* to the phosphine. The value of this coupling constant for **5e** ($^1J(PPt) = 2178$ Hz) is very close to that reported for $[PtMe(C_6H_4CH{=}NCH_2C_6H_4Cl)(PPh_3)]$ ($^1J(PPt) = 2175$ Hz) [14], while it is slightly larger for **5c** ($^1J(PPt) = 2217$ Hz).

A high field shift of the C_4 methoxy group resonance [3], as well as of the aromatic protons of the metallated ring signals [12], has been reported for related cyclopalladated compounds containing triphenylphosphine. This result has been attributed to the shielding effect caused by a phosphine phenyl ring according to a *cis* arrangement of these groups. However, for **5c** and **5e**, the triphenylphosphine and the metallated ring are mutually *trans*, and such high field shifts are not observed. As a

result, for **5c** the resonances due to the methoxy groups appear at $\delta = 3.69$ and 3.82 ppm, and for both **5c** and **5e** the resonances due to the aromatic protons of the metallated ring could not be unambiguously assigned since they are overlapped by the phosphine and the benzyl phenyl rings resonances.

The compound [PtMe(3-MeC$_6$H$_3$CH=NCH$_2$Ph)(PPh$_3$)] (**5e**) was also characterized crystallographically. Suitable crystals were grown by slow evaporation from an acetone–hexane solution. Atomic coordinates are given in Table 1, selected bond lengths and angles in Table 2, and crystallographic data in Table 3 and in Section 3.

The crystal structure is composed of discrete molecules separated by van der Waals distances. The structure is shown in Fig. 2 and confirms the features predicted from spectroscopic characterization and chemical evidence. The methyl group is *trans* to the nitrogen atom, and the C=N group is *endo* to the cycle. The metallation site is C_6 and the methyl group in the aryl ring is not adjacent to the metallation site.

The coordination sphere of platinum is square-planar with a tetrahedral distortion. The following displacements are observed from the least-squares plane of the coordination sphere: Pt, 0.032 Å; P, −0.153 Å; N, 0.162 Å; C(1), −0.201 Å; C(16), 0.159 Å. The metallacycle displays an envelope conformation with the Pt, N, C(1), C(7) moiety planar and the C(6) atom displaced from the plane by −0.088 Å. The angle between the coordination plane and the planar metallacycle moiety is 8.16°. The angles between adjacent atoms in the coordination sphere of platinum lie in the range 80.3(2)–97.30(13)°, the smallest angle corresponding to the metallacycle. Bond lengths in the coordination sphere of platinum are in the range expected for cyclometallated platinum(II) or platinum(IV) compounds [13–15].

Table 1
Atomic coordinates with estimated standard deviations in parentheses for non-hydrogen atoms for **5e**

	x ($\times 10^{-4}$)	y ($\times 10^{-4}$)	z ($\times 10^{-4}$)
Pt	2544(1)	3365(1)	1709(1)
P	3573(1)	2205(1)	3187(2)
N	1240(3)	2244(5)	1856(6)
C(1)	1593(3)	4100(4)	64(6)
C(2)	1695(4)	5008(5)	−991(8)
C(3)	954(5)	5269(6)	−2142(8)
C(4)	51(4)	4581(5)	−2334(7)
C(5)	−109(4)	3686(6)	−1366(7)
C(6)	648(4)	3458(5)	−180(7)
C(7)	512(4)	2506(6)	901(8)
C(8)	1131(5)	1384(9)	3063(12)
C(9)	122(4)	885(6)	3096(7)
C(10)	−358(6)	−281(7)	−2353(9)
C(11)	−1249(6)	−743(9)	−2451(13)
C(12)	−1689(6)	−61(10)	3316(12)
C(13)	−1231(7)	1072(10)	4084(11)
C(14)	−318(6)	1567(7)	3972(10)
C(15)	−885(2)	4876(2)	−3798(3)
C(16)	3632(4)	4723(5)	1556(9)
C(17)	3784(4)	2407(5)	5242(7)
C(18)	3193(5)	3060(6)	5866(10)
C(19)	3333(8)	3168(8)	7455(12)
C(20)	4063(9)	2700(9)	8414(10)
C(21)	4664(7)	2096(8)	7783(10)
C(22)	4532(5)	1942(8)	6214(9)
C(23)	3148(4)	502(56)	2676(7)
C(24)	2730(5)	142(6)	1150(8)
C(25)	2404(5)	−1121(7)	629(10)
C(26)	2547(6)	−2050(7)	1670(12)
C(27)	2930(6)	−1702(7)	3182(12)
C(28)	3255(5)	−429(6)	3716(8)
C(29)	4788(4)	2341(5)	2960(7)
C(30)	5059(5)	1426(7)	2136(9)
C(31)	5990(7)	1544(11)	1942(14)
C(32)	6634(5)	2575(9)	2602(13)
	6376(6)	3534(8)	3461(16)
C(34)	5448(5)	3400(7)	3618(11)

Table 2
Selected bond lengths (Å) and angles (°) for 5e

Bond lengths			
P–Pt	2.2717(14)	C(5)–C(4)	1.356(8)
N–Pt	2.141(4)	C(6)–C(5)	1.381(9)
C(1)–Pt	2.018(5)	C(2)–C(1)	1.406(7)
C(16)–Pt	2.028(5)	C(15)–C(4)	1.711(6)
C(17)–P	1.809(6)	C(7)–C(6)	1.466(7)
C(23)–P	1.824(5)	C(9)–C(8)	1.505(8)
C(29)–P	1.835(5)	C(10)–C(9)	1.383(11)
C(7)–N	1.255(9)	C(14)–C(9)	1.393(11)
C(8)–N	1.479(8)	C(11)–C(10)	1.356(12)
C(6)–C(1)	1.408(7)	C(11)–C(12)	1.39(2)
C(3)–C(2)	1.359(10)	C(12)–C(13)	1.35(2)
C(4)–C(3)	1.380(9)	C(13)–C(14)	1.398(13)
Bond angles			
C(1)–Pt–C(16)	91.5(2)	C(3)–C(4)–C(15)	119.6(4)
C(1)–Pt–N	80.3(2)	C(4)–C(5)–C(6)	119.2(5)
C(16)–Pt–N	168.5(2)	C(5)–C(6)–C(1)	123.0(5)
C(1)–Pt–P	168.3(2)	C(5)–C(6)–C(7)	121.3(5)
C(16)–Pt–P	92.3(2)	C(1)–C(6)–C(7)	115.8(5)
N–Pt–P	97.3(13)	N–C(7)–C(6)	118.4(5)
C(17)–P–C(23)	105.2(3)	N–C(8)–C(9)	116.9(6)
C(23)–P–C(29)	100.7(2)	C(10)–C(9)–C(14)	118.9(6)
C(17)–P–C(29)	103.1(3)	C(10)–C(9)–C(8)	121.4(7)
C(17)–P–Pt	118.0(2)	C(14)–C(9)–C(8)	119.6(8)
C(23)–P–Pt	110.1(2)	C(11)–C(10)–C(9)	120.6(8)
C(29)–P–Pt	117.8(2)	C(10)–C(11)–C(12)	120.4(9)
C(7)–N–C(8)	120.1(5)	C(13)–C(12)–C(11)	120.5(7)
C(7)–N–Pt	112.8(3)	C(12)–C(13)–C(14)	119.6(8)
C(8)–N–Pt	126.5(4)	C(9)–C(14)–C(13)	120.0(8)
C(2)–C(1)–C(6)	114.1(5)	C(22)–C(17)–P	120.8(5)
C(2)–C(1)–Pt	133.1(4)	C(18)–C(17)–P	120.1(5)
C(6)–C(1)–Pt	112.3(3)	C(24)–C(23)–P	116.4(4)
C(3)–C(2)–C(1)	123.7(5)	C(28)–C(23)–P	124.3(5)
C(2)–C(3)–C(4)	118.9(5)	C(30)–C(29)–P	122.2(5)
C(5)–C(4)–C(3)	121.0(6)	C(34)–C(29)–P	119.2(5)
C(5)–C(4)–C(15)	119.4(5)		

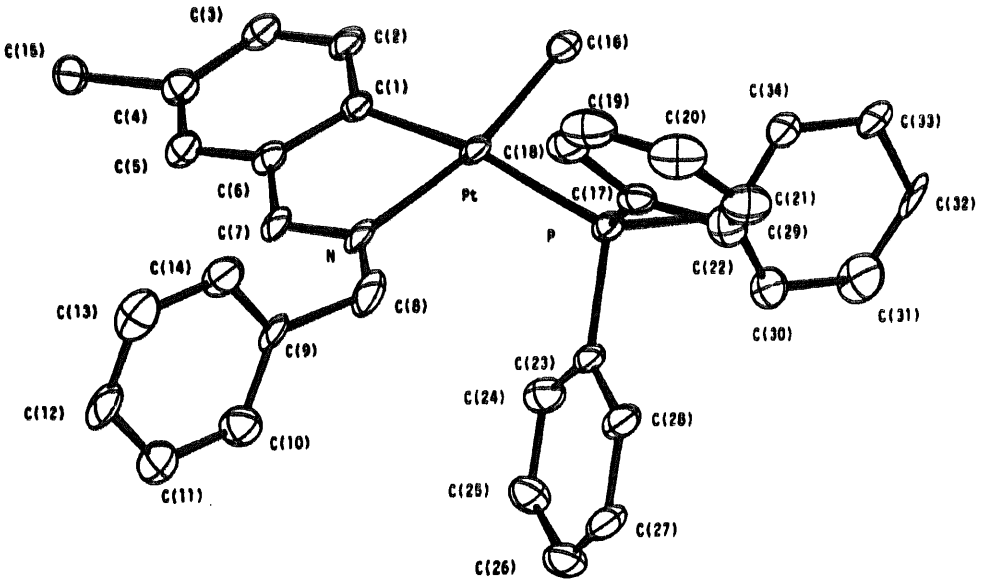


Fig. 2. View of the structure of 5e.

We have reported previously that the intramolecular C(aryl)–H bond activation at platinum is favoured when a fluorine atom occupies a position adjacent to this bond. In contrast, the presence of methoxy or methyl groups inhibits the metallation. For asymmetric ligands **2c** and **2e**, the metallation occurs regioselectively at the less hindered and less electron rich of the two *ortho* positions. A comparison of the stereo-electronic parameters of methyl, methoxy and fluorine groups is presented in Table 4 [16].

The methyl group is much bulkier than fluorine and steric effects could account for the results observed. Moreover, electronic effects of methyl groups do not favour the formation of platinacycles. The methoxy group is only slightly larger than fluorine, but their electronic properties differ, since the inductive electron-withdrawing effect of fluorine overcomes its unfavourable mesomeric effect while the reverse occurs for the methoxy group.

Table 4
Electronic and steric parameters for several substituents [a]

	σ_I	σ_R	E_S
F	0.50	−0.31	−0.46
Me	−0.05	−0.13	−1.24
OMe	0.27	−0.42	−0.55

[a] σ_I, σ_R and E_S are inductive (*para*), mesomeric (*para*) and steric parameters respectively, taken from [16]. H is taken as a standard, with a value 0. Positive σ values indicate electron-withdrawing groups; negative σ values indicate electron-donating groups; negative E_S values indicate unfavourable steric effects.

3. Experimental details

^1H and $^{31}P\{^1H\}$ NMR spectra were recorded using Varian Gemini 200 (^1H; 200 MHz), Bruker WP80SY (^{31}P; 32.4 MHz) and Varian XL 300FT (^{31}P; 121.4 MHz) spectrometers, and referenced to $SiMe_4$ (^1H) and H_3PO_4 (^{31}P). Microanalyses were performed by the Institut de Química Bio-Orgànica de Barcelona (Consejo Superior de Investigaciones Científicas), and by the Serveis Científico-Tècnics de la Universitat de Barcelona. Decomposition points were obtained with a Buchi 510 melting-point instrument.

Table 3
Crystallographic data and details of the refinements for **5e**

Formula	$C_{34}H_{32}NPPt$
Formula weight	680.87
Crystal system; space group	Triclinic; $P\bar{1}$
a (Å)	14.661(2)
b (Å)	10.612(2)
c (Å)	9.087(2)
α (°)	92.17(2)
β (°)	105.59(2)
γ (°)	98.28(2)
V (Å^3)	1343.2(4)
D_c (g cm^{-3})	1.683
Z	2
F(000)	672
Crystal size (mm)	0.1×0.1×0.2
μ (Mo Kα) (cmSi)	53.07
λ (Mo Kα) (Å)	0.71069
T (K)	293(2)
Number of reflections collected	11588
R	0.049
$wR(F^2)$	0.114
Number of refined parameters	336
Maximum difference peak; minimum difference peak (electrons Å^{-3})	2.864; −2.121

3.1. Preparation of the compounds

The complex $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (**1**) was prepared by the method reported in the literature [17].

3.1.1 Compounds 2

These compounds were prepared by the reaction of 5 mmol of the corresponding aldehyde with the equimolecular amount of the benzylamine in ethanol [18]. The mixture was refluxed for 2 h and the solvent was removed in a rotary evaporator to yield yellow oils or white solids.

2,4,6-$(OMe)_3C_6H_2CH{=}NCH_2C_6H_5$ (2a). ^1H NMR ($CDCl_3$): δ 3.84 (s, OMe, 6H), 3.88 (s, OMe, 3H), 4.83 (s, CH_2), {6.13 (s, 2H), 7.33 (m), aromatics}, 8.63 (s, CHN) ppm.

3,5-$(OMe)_2C_6H_3CH{=}NCH_2C_6H_5$ (2b). ^1H NMR ($CDCl_3$): δ 3.82 (s, OMe), 4.83 (s, CH_2), {6.55 (s, 1H), 6.95 (s, 2H), 7.34 (m), aromatics}, 8.32 (s, CHN) ppm.

3,4-$(OMe)_2C_6H_3CH{=}NCH_2C_6H_5$ (2c). ^1H NMR ($CDCl_3$): δ 3.93 (s, OMe), 3.95 (s, OMe), 4.82 (s, CH_2), {6.91 (s, 2H), 7.26 (m), 7.36 (m), aromatics}, 8.25 (s, CHN) ppm.

2,5-$Me_2C_6H_3CH{=}NCH_2C_6H_5$ (2d). ^1H NMR ($CDCl_3$): δ 2.32 (s, *Ar*–Me) 2.47 (s, *Ar*–Me), 4.84 (s, CH_2), {7.11 (m), 7.36 (m), 7.70 [s], aromatics}, 8.70 (s, CHN) ppm.

3-$MeC_6H_4CH{=}NCH_2C_6H_5$ (2e). ^1H NMR ($CDCl_3$): δ 2.42 (s, *Ar*–Me), 4.86 (s, CH_2), {7.30 (s, 2H), 7.56 (d), 7.69 (s), aromatics}, 8.40 (s, CHN) ppm.

3.1.2. Compounds 3

These compounds were detected using the following procedure: 20.0 mg (0.035 mmol) of the compound $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (**1**) and 0.08 mmol of the corresponding imine were dissolved in 0.7 ml of acetone-d_6 and the ^1H NMR spectrum was recorded.

$[PtMe_2\{2,4,6\text{-}(OMe)_3C_6H_2CH{=}NCH_2Ph\}(SMe_2)]$ (3a). ^1H NMR (acetone-d_6): δ 0.08 (s, ^2J(HPt) = 85 Hz, Me), 0.36 (s, ^2J(HPt) = 86 Hz, Me),

1.49 (s, ^3J(HPt) = 25 Hz, SMe_2), 3.82 (s, OMe), 3.86 (s, OMe), 5.02 (s, ^3J(HPt) = 25 Hz, CH_2), {7.41 (m) 7.59 (m), aromatics}, 8.87 (s, ^3J(HPt) = 51 Hz, CHN) ppm.

[$PtMe_2${3,5-$(OMe)_2C_6H_3CH=NCH_2Ph$}(SMe_2)] (3b). ^{1}H NMR (acetone-d_6): δ 0.33 (s, ^2J(HPt) = 86 Hz, Me), 0.36 (s, ^2J(HPt) = 85 Hz, Me), 1.63 (s, ^3J(HPt) = 25 Hz, SMe_2), 3.70 (s, OMe), [4.90 (d), 5.20 (d), ^2J(HH) = 13 Hz, CH_2, *AB* pattern], {6.50 (m), 6.70 (m), 7.31 (m), 7.80 (m), aromatics}, 9.10 (s, ^3J(HPt) = 48 Hz, CHN) ppm.

[$PtMe_2$(2,5-$Me_2C_6H_3CH=NCH_2Ph$)(SMe_2)] (3d). ^{1}H NMR (acetone-d_6): δ 0.21 (s, ^2J(HPt) = 80 Hz, *Pt*–Me), 0.38 (s, ^2J(HPt) = 86 Hz, *Pt*–Me), 1.48 (s, ^3J(HPt) = 23 Hz, SMe_2), 2.24 (s, *Ar*–Me), 2.29 (s, *Ar*–Me), 9.40 (s, ^3J(HPt) = 45 Hz, CHN) ppm.

3.1.3. Compounds 4

These compounds were prepared by reaction of 100 mg (0.17 mmol) of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (1) with 0.35 mmol of the corresponding imine in acetone. The mixture was stirred for 16 h and the solvent was removed in a rotary evaporator. The residue was washed with hexane and recrystallized in acetone–hexane to yield yellow–orange solids, which were filtered and washed with hexane.

[PtMe{3,4-$(OMe)_2C_6H_2CH=NCH_2C_6H_5$}$(SMe_2)$] (4c). Yield, 110 mg (60%); melting point (m.p.), 87°C (decomposition). Anal. Found: C, 42.72; H, 4.66; N, 2.60. $C_{19}H_{25}NO_2SPt$ calc.: C, 43.34; H, 4.79; N, 2.66%. ^{1}H NMR (acetone-d_6): δ 0.80 (s, ^2J(HPt) = 83 Hz, Me), 1.95 (s, ^3J(HPt) = 30 Hz, SMe_2), 3.71 (s, OMe), 3.81 (s, OMe), 5.10 (s, ^3J(HPt) = 14 Hz, CH_2), {7.09 (m), 7.29 (m), aromatics}, 8.61 (s, ^3J(HPt) = 57 Hz, CHN) ppm.

[PtMe(3-$MeC_6H_3CH=NCH_2C_6H_5$)(SMe_2)] (4e). Yield, 110 mg (66%); m.p., 112°C (decomposition). Anal. Found: C, 45.10; H, 4.90; N, 3.20 $C_{18}H_{23}NSPt$ calc.: C, 44.99; H, 4.82; N, 2.9%. ^{1}H NMR (acetone-d_6): δ 0.83 (s, ^2J(HPt) = 83 Hz, *Pt*–Me), 1.98 (s, ^3J(HPt) = 27 Hz, SMe_2), 2.19 (s, *Ar*–Me), 5.15 (s, ^3J(HPt) = 15 Hz, CH_2), {7.10 (m), 7.32 (m), 7.50 (m) aromatics}, 8.70 (s, ^3J(HPt) = 56 Hz, CHN) ppm.

3.1.4. Compounds 5

These compounds were prepared by reaction of 50 mg of the corresponding compound 4 with the equimolecular amount of PPh_3 in acetone. The mixture was stirred at room temperature for 16 h. On addition of hexane, yellow crystals were formed, and they were collected by filtration, washed with hexane and dried in vacuo.

[PtMe{3,4-$(OMe)_2C_6H_2CH=NCH_2C_6H_5$}$(PPh_3)$] (5c). Yield, 50 mg (73%); m.p., 117°C (decomposition). Anal. Found: C, 57.21; H, 4.82; N, 1.84. $C_{35}H_{34}NO_2PPt$ calc.: C, 57.84; H, 4.71; N, 1.93%. ^{1}H NMR(acetone-d_6): δ 0.62 (d, ^2J(HPt) = 84 Hz, ^3J(HPt) = 7 Hz, Me), 3.69 (s, OMe), 3.82 (s, OMe), 4.25 (s, ^3J(HPt) = 10 Hz, CH_2), {6.89 (m), 7.07 (m), 7.39 (m), aromatics}, 8.34 (s, ^3J(HPt) = 58 Hz, CHN) ppm. ^{31}P NMR (acetone): δ = 31.71 (s, ^1J(PPt) = 2217 Hz) ppm.

[PtMe(3-$MeC_6H_3MeCH=NCH_2C_6H_5$)(PPh_3)] (5e). Yield, 55 mg (78%); m.p., 205–208°C (decomposition). Anal. Found: C, 60.28; H, 4.35; N, 2.10. $C_{34}H_{32}NPPt$ calc.: C, 59.99; H, 4.74; N, 2.06%. ^{1}H NMR(acetone-d_6): δ 0.64 (d, ^2J(HPt) = 84 Hz, ^3J(HPt) = 7 Hz, *Pt*–Me), 2.19 (s, *Ar*–Me), 4.31 (s, ^3J(HPt) = 10 Hz, CH_2), {6.90 (m, 1H), 7.16 (m), 7.39 (m), 7.60 (m), aromatics}, 8.43 (s, ^3J(HPt) = 56 Hz, CHN) ppm. ^{31}P NMR (acetone), δ 31.85 (s, ^1J(PPt) = 2178 Hz) ppm.

3.2. X-ray structure analysis

3.2.1. Data collection

A prismatic crystal (0.1 × 0.1 × 0.2 mm) was selected and mounted on a Philips PW-1100 diffractometer. Unit-cell parameters were determined from automatic centring of 25 reflections ($8° \leq \theta \leq 12°$) and refined by the least-squares method. Intensities were collected with graphite monochromated Mo Kα radiation, using the ω–2θ scan technique. 11 588 reflections were measured in the range $2.24° \leq \theta \leq 35.40°$, 6853 of which were assumed as observed applying the condition $I \geq 2\sigma(I)$. Three reflections were measured every 2 h as orientation and intensity control; significant intensity decay was not observed. Lorentz–polarization and absorption corrections were made. Further details are given in Table 3.

3.2.2. Structure solution and refinement

The structure was solved by Patterson synthesis, using the SHELXS computer program [19] and refined by the full-matrix least-squares method, with the SHELX93 computer program [20], using 9505 reflections (very negative intensities were not considered). The function minimized was $\Sigma w[|F_0|^2 - |F_c|^2]^2$, where $w = [\sigma^2(I) + (0.0876P)]^{-1}$ and $P = (|F_0|^2 + 2|F_c|^2)/3$. f, f' and f'' were taken from the *International Tables of X-ray Crystallography* [21]. All H atoms were computed and refined with an overall isotropic temperature factor, using a riding model. The final R factor, the number of parameters refined and the maximum and minimum peaks in the final difference synthesis are given in Table 3.

Tables of hydrogen atom coordinates, anisotropic thermal parameters and complete lists of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

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