

Factors affecting the lability of the $\sigma(\text{M}-\text{X})$ bond in cycloplatinated and cyclopalladated complexes containing $[\text{C}(\text{sp}^2, \text{ferrocene}), \text{N}, \text{X}]^-$ or $[\text{C}(\text{sp}^2, \text{phenyl}), \text{N}, \text{X}]^-$ ($\text{X} = \text{S}, \text{N}$) terdentate ligands

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Received 11 June 2004; accepted 1 July 2004

Available online 6 August 2004

Abstract

The reactions of the cyclometallated complexes $[\text{M}\{[(\eta^5\text{-C}_5\text{H}_3)\text{-CH=N-(C}_6\text{H}_4\text{-2-SMe)]Fe}(\eta^5\text{-C}_5\text{H}_5)\}\text{Cl}]$ [with $\text{M} = \text{Pt}$ (**5a**) or Pd (**5b**)] with PPh_3 under different experimental conditions are reported. These studies have allowed the isolation of $[\text{M}\{[(\eta^5\text{-C}_5\text{H}_3)\text{-CH=N-C}_6\text{H}_4\text{-2-SMe)]Fe}(\eta^5\text{-C}_5\text{H}_5)\}(\text{PPh}_3)]\text{X}$ [$\text{M} = \text{Pt}$ and $\text{X}^- = \text{Cl}^-$ (**6a**) or BF_4^- (**7a**) or $\text{M} = \text{Pd}$ and $\text{X}^- = \text{Cl}^-$ (**6b**) or BF_4^- (**7b**)] and the neutral complex $[\text{Pd}\{[(\eta^5\text{-C}_5\text{H}_3)\text{-CH=N-(C}_6\text{H}_4\text{-2-SMe)]Fe}(\eta^5\text{-C}_5\text{H}_5)\}\text{Cl}(\text{PPh}_3)]$ (**8b**). In **6–7a,b** the ferrocenyl Schiff base behaves as a $[\text{C}(\text{sp}^2, \text{ferrocene}), \text{N}, \text{S}]^-$ group while in **8b** it acts as a $[\text{C}(\text{sp}^2, \text{ferrocene}), \text{N}]^-$ ligand. The X-ray crystal structure of **7b** confirms the mode of binding of the ferrocenyl ligand. The comparison of the results obtained and those reported for $[\text{M}\{(\text{C}_6\text{H}_4)\text{-CH=N-(CH}_2\text{-CH}_2\text{-2-SEt)}\}\text{Cl}]$ and $[\text{M}\{(\text{C}_6\text{H}_4)\text{-CH=N-(C}_6\text{H}_4\text{-2-SMe)}\}\text{Cl}]$ {with a $[\text{C}(\text{sp}^2, \text{phenyl}), \text{N}, \text{S}]^-$ terdentate ligand} or $[\text{M}\{[(\eta^5\text{-C}_5\text{H}_3)\text{-CH=N-(CH}_2\text{)}_3\text{-NMe}_2]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}\text{Cl}]$ {in which the ligand acts as a $[\text{C}(\text{sp}^2, \text{ferrocene}), \text{N}, \text{N}']^-$ group} have allowed the elucidation of the relative importance of the factors affecting the lability of the $\text{M}-\text{X}$ ($\text{X} = \text{S}$ or N') and $\text{M}-\text{Cl}$ bonds in cyclometallated compounds with $[\text{C}, \text{N}, \text{S}]^-$ and $[\text{C}(\text{sp}^2, \text{ferrocene}), \text{N}, \text{X}]^-$ ligands.

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Keywords: Cyclometallation; Ferrocene; Platinacycles; Palladacycle

1. Introduction

Cyclometallated complexes containing platinum(II) or palladium(II) ligands [1] have generated considerable interest since long ago mainly due to their applications in homogeneous catalysis or for the design of new materials with outstanding properties [1–18]. Their utility as precursors in organic and organometallic synthesis

[13–18] is also well-known. Among all the examples reported so far, those containing $[\text{C}, \text{N}, \text{X}]^-$ ($\text{X} = \text{N}', \text{O}$ or S) terdentate groups with three donor atoms of different hardness [19], are particularly interesting because the ligand may adopt different binding modes and hapticities {i.e. $(\text{C}, \text{N}, \text{X})^-$, $(\text{C}, \text{N})^-$, $(\text{C})^-$ } and the study of the factors that affect the ease with which these changes occur is relevant from the point of view of their potential utility in homogeneous catalysis.

Most of the articles reported so far involve the study of the lability of the $\sigma(\text{M}-\text{X})$ bonds of cyclometallated

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complexes $[M(C,N,X)Cl]$ ($M = Pt$ or Pd and $X = N'$ or O) containing a $\sigma[M-C(sp^2, \text{aryl})]$ bond or to a lesser extent a $\sigma[M-C(sp^3)]$ bond [20–22], but related studies on metallacycles in which palladium(II) or platinum(II) are bound to a $C(sp^2, \text{ferrocene})$ atom are less common [23,24]. To the best of our knowledge, only the reactivity of compounds: $[M\{[(\eta^5-C_5H_3)-CH=N-(CH_2)_n-NMe_2]Fe(\eta^5-C_5H_4)\}Cl]$ {with $n = 3$, $M = Pt$ (**1a**) or Pd (**1b**) or $n = 2$, $M = Pd$ (**2b**)} (Fig. 1(a)) [23,24] with PPh_3 has been reported. Besides that, parallel studies involving platina- or palladacycles with a $[C,N,S]^-$ terdentate group are scarce [25–27] and the examples reported so far are practically restricted to: $[M\{(C_6H_5)-CH=N-(CH_2-CH_2-2-SEt)\}Cl]$ { $M = Pt$ (**3a**), Pd (**3b**)} and $[M\{(C_6H_5)-CH=N-(C_6H_4-2-SMe)\}Cl]$ { $M = Pt$ (**4a**), Pd (**4b**)} (Fig. 1(b) and (c)) which contain a $[C(sp^2, \text{phenyl}), N, S]^-$ ligand [25,26]. Compounds **3–4a,b** undergo the cleavage of the $M-S$ bond in the presence of PPh_3 . In the view of this and in order to clarify the influence of the type of metallated carbon in a *trans*-arrangement to the $M-S$ bond on the lability of this link, we were prompted to study the reactions of $[M\{[(\eta^5-C_5H_3)-CH=N-(C_6H_4-2-SMe)]Fe(\eta^5-C_5H_5)\}Cl]$ { $M = Pt$ (**5a**), Pd (**5b**)} [28] (Fig. 1(d)) with PPh_3 .

2. Results and discussion

Treatment of $[Pt\{[(\eta^5-C_5H_3)-CH=N-(C_6H_4-2-SMe)]Fe(\eta^5-C_5H_5)\}Cl]$ (**5a**) with the equimolar amount

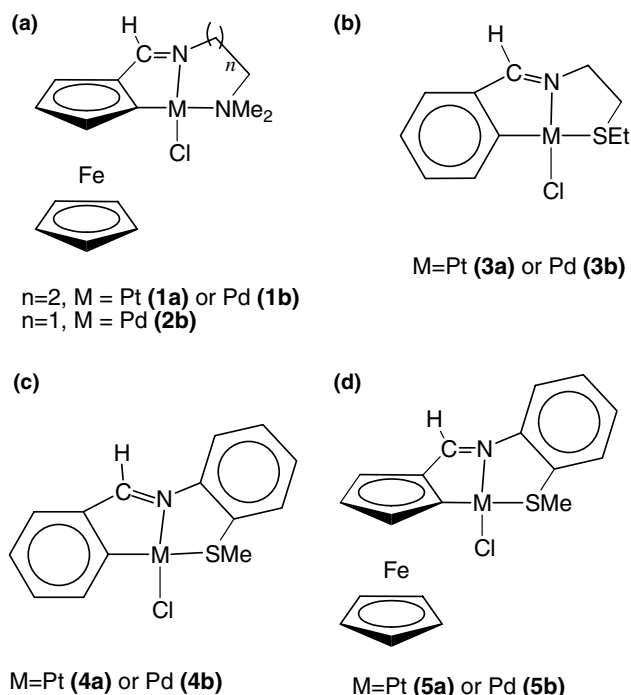


Fig. 1.

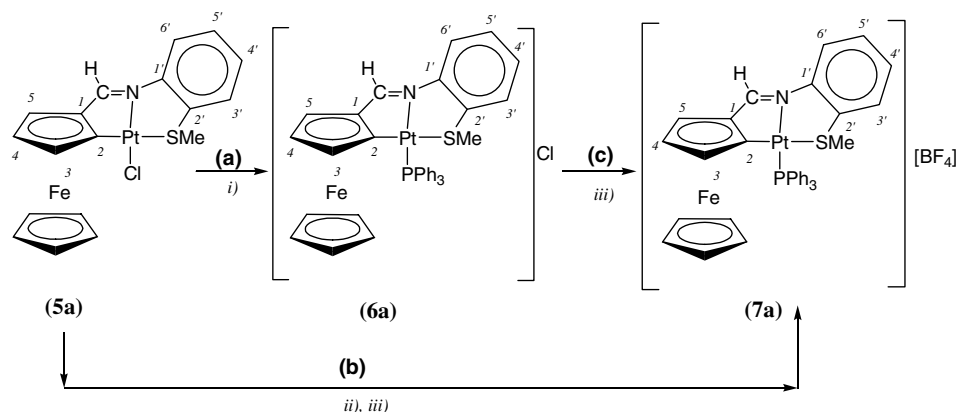
of PPh_3 in CH_2Cl_2 at ca. 20 °C for 1 h, followed by concentration to dryness, gave a deep purple solid, which was identified according to its elemental analyses and (FAB⁺) mass spectrum as $[Pt\{[(\eta^5-C_5H_3)-CH=N-(C_6H_4-2-SMe)]Fe(\eta^5-C_5H_5)\}(PPh_3)]Cl$ (**6a**) [Scheme 1, step (a)]. Its infrared spectrum showed the typical bands due to the coordinated PPh_3 ligand [29,30] and a sharp and intense band at ca. 1533 cm^{-1} assigned to the stretching of the imine group.

The $^{195}Pt\{^1H\}$ NMR spectrum of **6a** (in $CDCl_3$ at 300 K) showed a doublet at $\delta = -4449$ ppm ($^1J_{P-Pt} = 3785$ Hz) which is consistent with the values reported for related platinacycles with a $[C,N,S]^-$ terdentate group [25–27,31] and its $^{31}P\{^1H\}$ NMR spectrum suggested a *cis*-arrangement between the metallated carbon and the phosphine ligand, in good agreement with the *trans*-phobia effect [32].

In the 1H NMR spectrum of **6a** at 300 K the signals due to the protons of the SMe and $(\eta^5-C_5H_5)$ groups were broad (Fig. 2(a)). This finding could be indicative of a dynamic process in solution (possibly involving the $-SMe$ moiety). In order to confirm this hypothesis, 1H and $^{31}P\{^1H\}$ NMR studies were carried out in the range 230–300 K. At 230 K, the 1H NMR spectrum, showed two sets of superimposed signals of relative intensities 2.1:1.0 (Fig. 2(b)) and the positions of the two signals observed in the $^{31}P\{^1H\}$ NMR spectrum [Fig. 3] were consistent with the values expected for platinacycles with a PPh_3 ligand in a *trans*-arrangement to the imine nitrogen [20,25a,26]. The coalescence of the two signals observed in the $^{31}P\{^1H\}$ NMR spectra was achieved at 270 K (Fig. 3). These findings suggested the presence of two different platinum(II) complexes (in a molar ratio = 2.1) in $CDCl_3$ solution.

It has been reported that some platinacycles with terdentate $[C(sp^2, \text{phenyl}), N, N']^-$ ligands, such as $[Pt\{(C_6H_4)-CH=N-(CH_2)_2-NMe_2\}(PPh_3)]Cl$, undergo a fast exchange process in solution which involves the cleavage of the terminal $Pt-NMe_2$ bond and the formation of a $Pt-Cl$ bond [Scheme 2(a)] [20]. In order to elucidate if the two species present in $CDCl_3$ solutions of **6a** could also be related by a change in the mode of binding of the ferrocenyl ligand {from $[C(sp^2, \text{ferrocene}), N, S]^-$ (in **6a**) to $[C(sp^2, \text{ferrocene}), N]^-$ (in **6a')**} [Scheme 2(b)], we prepared $[Pt\{[(\eta^5-C_5H_3)-CH=N-(C_6H_4-2-SMe)]Fe(\eta^5-C_5H_5)\}(PPh_3)][BF_4]$ (**7a**) and studied its solution behaviour in $CDCl_3$.

Complex **7a** was synthesized either from **5a** in the presence of $Tl[BF_4]$ followed by the removal of $TlCl$ and the subsequent addition of PPh_3 , or from **6a** using $Tl[BF_4]$ to remove the chloro ligand bound to the platinum(II) [Scheme 1, steps (b) and (c)]. Proton and $^{31}P\{^1H\}$ NMR spectra of a $CDCl_3$ solution of **7a** in the range 230–300 K were identical to those obtained for **6a**. Thus, indicating that the Cl^- (in **6a**) or the $[BF_4]^-$ (in **7a**) anions were not involved in the dynamic



Scheme 1. (i) PPh_3 in CH_2Cl_2 at room temperature. (ii) $\text{Ti}[\text{BF}_4]$ in acetone, followed by removal of the TiCl formed (iii) addition of the stoichiometric amount of PPh_3 .

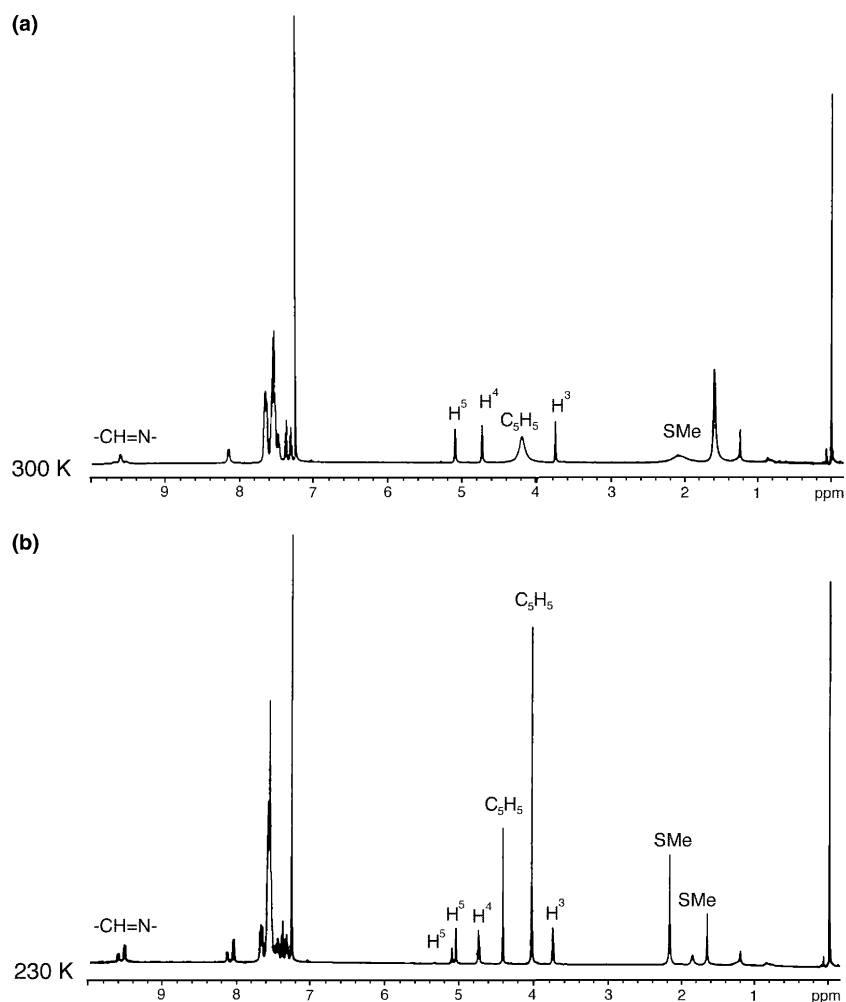


Fig. 2. ^1H NMR spectra (500 MHz) of $[\text{Pt}\{(\eta^5\text{-C}_5\text{H}_5)\text{-CH=N-(C}_6\text{H}_4\text{-2SMe)}\}(\eta^5\text{-C}_5\text{H}_5)\}(\text{PPh}_3)]\text{Cl}$ (**6a**) in CDCl_3 at $T = 300$ K (a) and 230 K (b).

process. The $^31\text{P}\{^1\text{H}\}$ NMR spectrum of **6a** and **7a** at low temperatures suggested that the environment of the platinum(II) should be very similar in the two species. Besides that, $\{^1\text{H}\text{--}^1\text{H}\}$ NOESY and ROESY spectra of **7a** at 230 K revealed that the two complexes

interchanged in solution and differed in the relative arrangement of: (a) the Me group of the --SMe moiety and one of the phenyl rings of the PPh_3 and (b) the C_5H_5 ring and another C_6H_5 group of the coordinated phosphine.

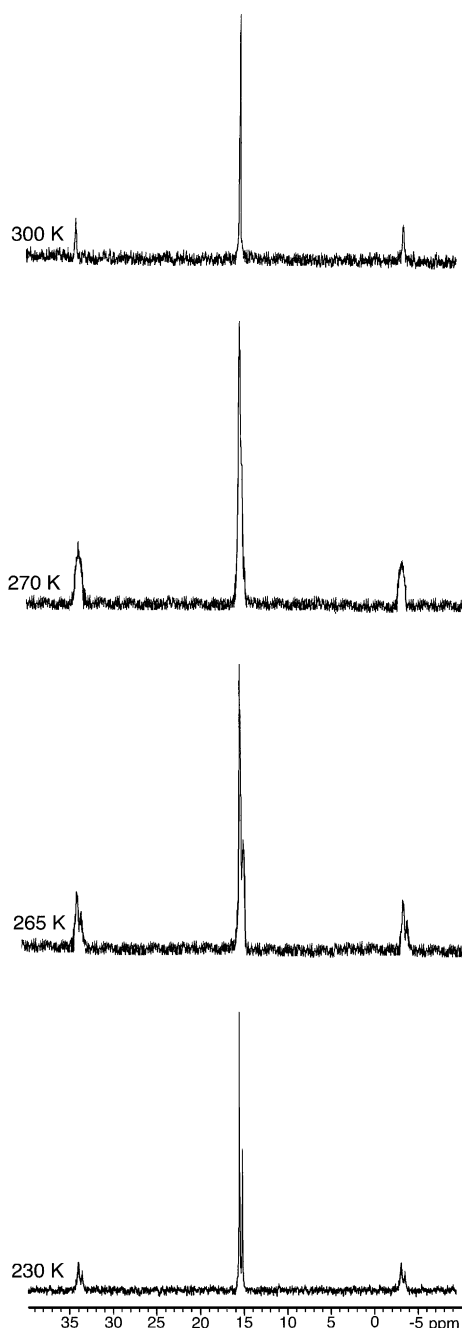


Fig. 3. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (250 MHz) of $[\text{Pt}\{[(\eta^5\text{-C}_5\text{H}_5)\text{-CH=N-(C}_6\text{H}_4\text{-2SMe)]Fe}(\eta^5\text{-C}_5\text{H}_5)\}(\text{PPh}_3)]\text{Cl}$ in CDCl_3 at 300, 270, 265 and 230 K.

The results obtained in the reaction of **5a** with PPh_3 are in sharp contrast with those reported for $[\text{Pt}\{[(\eta^5\text{-C}_5\text{H}_5)\text{-CH=N-(CH}_2\text{-CH}_2\text{-CH}_2\text{-NMe}_2)]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}\text{-Cl}]$ (**1a**), $[\text{Pt}\{(\text{C}_6\text{H}_4)\text{-CH=N-(CH}_2\text{-CH}_2\text{-2-SEt)}\}\text{Cl}]$ (**3a**) and $[\text{Pt}\{(\text{C}_6\text{H}_4)\text{-CH=N-(C}_6\text{H}_4\text{-2-SMe)}\}\text{Cl}]$ (**4a**) for which the addition of the equimolar amount of PPh_3 in CH_2Cl_2 at room temperature produced the cleavage of the Pt–N_{amine} (in **1a**) or Pt–S (in **3a** and **4a**) bonds [Scheme 3(a)–(c)] [25b,26]. Thus, suggesting

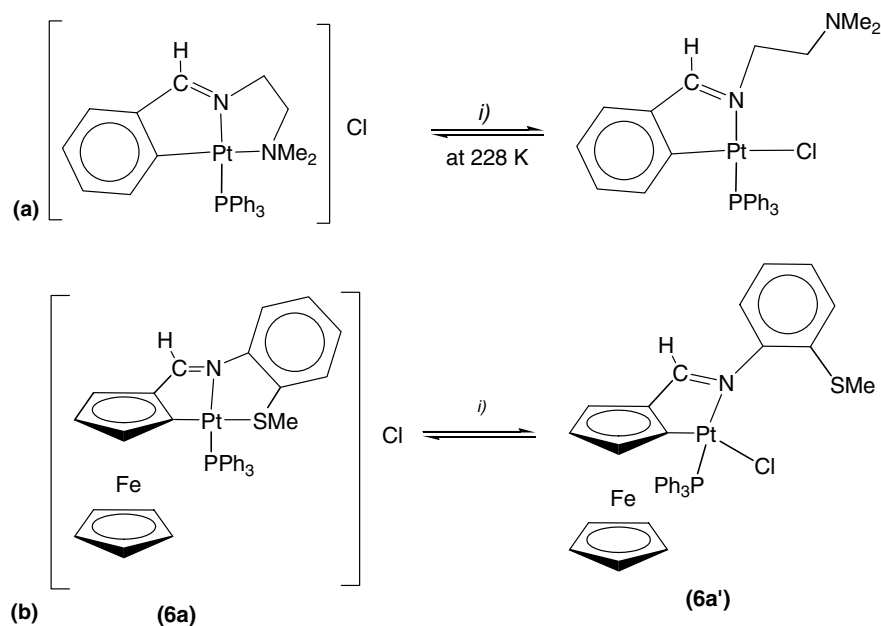
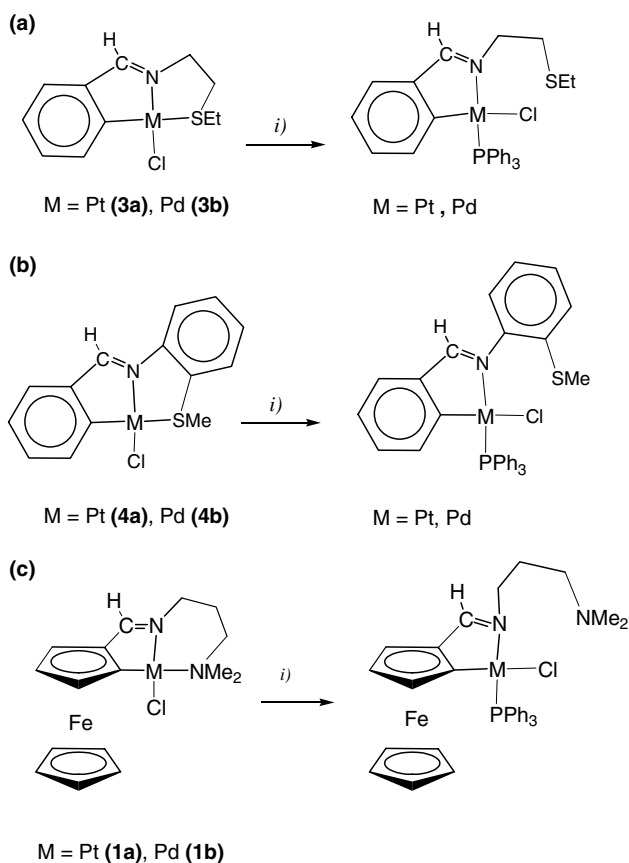
that in **5a** the Pt–S bond is less prone to cleave than in **3a** or **4a** or than the Pt–N_{amine} bond in **1a**.

The use of more severe experimental conditions (PPh_3 : Pt molar ratios varying from 1 to 3; in acetone or benzene, at room temperature or under reflux and with reaction periods up to 24 h) did not produce the cleavage of the Pt–S bond in **5a** or **6a**. In order to compare the reactivity of the M–Cl and M–S bonds in **5a** and **5b**, a parallel study was performed with the palladium(II) complex. When **5b** was treated with the equimolar amount of PPh_3 in CH_2Cl_2 at ca. 20 °C for 1 h, followed by the work up, a purple residue was isolated. Its ^1H NMR spectrum in CDCl_3 revealed the presence of **5b** and $[\text{Pd}\{[(\eta^5\text{-C}_5\text{H}_5)\text{-CH=N-(C}_6\text{H}_4\text{-2-SMe)]Fe}(\eta^5\text{-C}_5\text{H}_5)\}(\text{PPh}_3)]\text{Cl}$ (**6b**) [Scheme 4, step (a)] in a molar ratio = 1.0:0.3. Its $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum showed the signal of the free PPh_3 {at $\delta = -6.0$ ppm} and an additional singlet at 34.9 ppm, ascribed to complex **6b** (see below).

These findings are in contrast with those described for **3b** and **4b** for which the addition of PPh_3 (in a Pd: PPh_3 molar ratio = 1) produced the cleavage of the Pd–S bond [24b,25c]. Thus indicating a smaller lability of the Pd–S bond in **5b** when compared with those of **4b** and **3b**. This trend, which is similar to that described above for the platinum(II) derivatives, can be ascribed to the different *trans*-influence of the metallated carbon atom: a $\text{C}(\text{sp}^2, \text{ferrocene})$ atom (in **5b**) or a $\text{C}(\text{sp}^2, \text{phenyl})$ atom in **3b** and **4b**. Besides that, the comparison of the results obtained reveal that **5b** is less reactive than **5a** in front of PPh_3 .

When larger excesses of PPh_3 were used (molar ratio PPh_3 :**5b** = 1.5) the relative proportion **5b**:**6b** decreased and **6b** could be isolated in a higher yield. Complex **6b** was characterised by elemental analyses, mass spectra, infrared and NMR spectroscopy (see Section 4). The most outstanding features observed in the ^1H NMR spectrum of **6b** are: (a) the presence of a doublet due to phosphorous coupling at $\delta = 9.47$ ppm [$J_{\text{P-H}} = 8.5$ Hz], which is assigned to the imine proton and (b) the resonances of the H^3 and SMe protons appeared high-field shifted when compared with those of **5b** or the free ligand due to the paramagnetic anisotropy of the phenyl rings of the PPh_3 ligand. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **6b** [$\delta = 34.9$ ppm] was consistent with a *cis*-arrangement of the PPh_3 ligand and the metallated carbon of the ferrocenyl moiety, in good agreement with the *transphobia* effect [32]. ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **6b** (in CDCl_3) did not vary substantially in the range: 230–300 K.

For comparison purposes we also prepared and characterised compound: $[\text{Pd}\{[(\eta^5\text{-C}_5\text{H}_5)\text{-CH=N-(C}_6\text{H}_4\text{-2-SMe)]Fe}(\eta^5\text{-C}_5\text{H}_5)\}(\text{PPh}_3)]\text{[BF}_4\text{]}^-$ (**7b**) (Scheme 4, step (b) and Section 4). Its molecular structure consists of equimolar amounts of $[\text{Pd}\{[(\eta^5\text{-C}_5\text{H}_5)\text{-CH=N-(C}_6\text{H}_4\text{-2-SMe)]Fe}(\eta^5\text{-C}_5\text{H}_5)\}(\text{PPh}_3)]^+$, $[\text{BF}_4]^-$ anions and

Scheme 2. (i) CDCl_3 .Scheme 3. (i) PPh_3 in CH_2Cl_2 at room temperature.

CH_2Cl_2 . The ORTEP diagram of the cation together with the atom numbering scheme is depicted in Fig. 4.

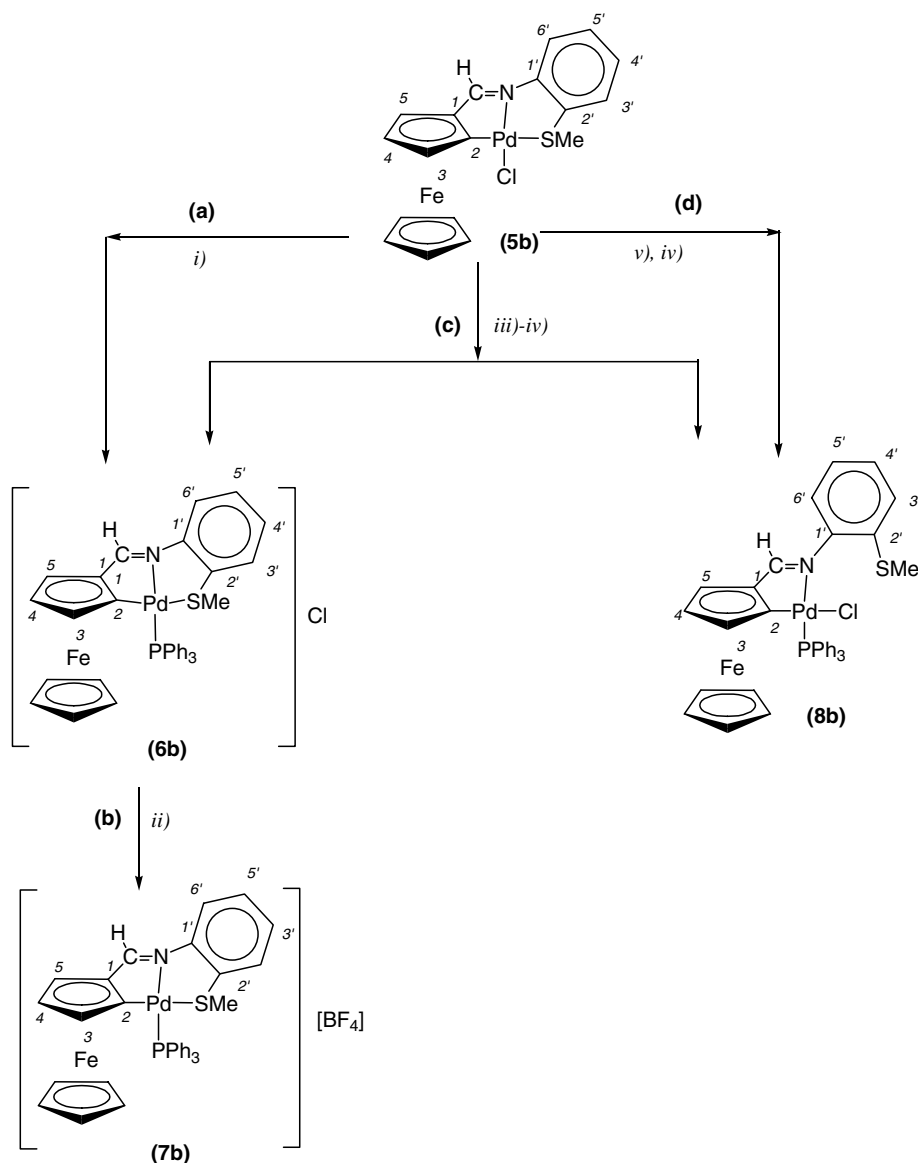
In the cation, the palladium(II) is bound to the two heteroatoms of the ferrocenyl ligand {N and S} and to

the C(6) atom of the 1,2-disubstituted pentagonal ring, thus confirming that the ligand acts as a $[\text{C}(\text{sp}^2, \text{ferrocene}), \text{N}, \text{S}]^-$ terdentate group. The fourth coordination site is occupied by the phosphorous atom of the PPh_3 group and a slightly distorted square-planar environment is the result.

The Pd–C(6) [2.001(3) Å], Pd–N [2.070(2) Å] and Pd–S [2.3750(2) Å] bond lengths are larger than the values reported for $[\text{Pd}\{(\eta^5\text{-C}_5\text{H}_5)\text{-CH=N-(C}_6\text{H}_4\text{-2-SMe)}\}\text{-Fe}(\eta^5\text{-C}_5\text{H}_5)\}\text{Cl}]$ (**5b**) [Pd–C(6), 1.978(5) Å; Pd–N, 2.020(3) Å and Pd–S, 2.3653(11) Å][28]. The cation contains a [5,5,5,6] tetracyclic system formed by the 1,2-disubstituted pentagonal ring of the ferrocenyl unit, a five-membered metallacycle, the chelate ring, formed by the binding of the two heteroatoms to the palladium, and the phenyl ring. The metallacycle, which contains the $>\text{C=N-}$ functional group (*endocyclic*), is twisted on the Pd–C(6) bond and the five-membered chelate ring is twisted on the Pd–S bond. Bond lengths and angles of the “ $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)$ ” moiety are consistent with those reported for most ferrocene derivatives [33]. The two pentagonal rings are planar (*tilt angle* = 2.7°) and they deviate by ca. 2.1° from the ideal eclipsed conformation.

The separation between the C(18)–H(18A) bond of one cation and the phenyl ring formed by the set of atoms [C(25)–C(30)] of a neighbouring unit is 2.660 Å, which suggests a C–H $\cdots\pi$ interaction.

More interesting were the results obtained when **5b** was treated with PPh_3 (in a PPh_3 :**5b** molar ratio = 1.5) for 1 h in benzene or acetone under reflux. In this case, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the crude showed three singlets at $\delta = -6.0$, 34.8 and 38.1 ppm. The two signals at higher fields are due to the free PPh_3 and to **6a**,



Scheme 4. (i) PPh_3 in CH_2Cl_2 at room temperature. (ii) $\text{Ti}[\text{BF}_4]$ in acetone. (iii) PPh_3 (molar ratio $\text{PPh}_3:\text{Pd} = 1.5$) in benzene under reflux for 1 h. (iv) SiO_2 column chromatography (v) PPh_3 (molar ratio $\text{PPh}_3:\text{Pd} = 1.5$) in benzene under reflux for 24 h.

respectively. The chemical shift of the remaining signal [$\delta = 38.2$ ppm] was very similar to those reported for palladacycles: $[\text{Pd}\{[(\eta^5\text{-C}_5\text{H}_5)\text{-CH=N-R}^1]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}\text{Cl}(\text{PPh}_3)]$ with (R^1 = phenyl, benzyl or naphthyl groups) in which the ferrocenyl Schiff base behaves as a $[\text{C}(\text{sp}^2, \text{ferrocene}), \text{N}]^-$ group [34]. Thus, suggesting the presence of a new cyclopalladated derivative, here in after referred to as **8b** [Scheme 4, step (c)]. The ^1H NMR spectrum at 300 K revealed that the two palladium(II) compounds coexisted in a **8b:6b** molar ratio = 0.13. This ratio increased for longer reaction periods and when reaction was carried out in refluxing benzene for 24 h, **8b** was isolated in a fairly good yield [Scheme 4, step (d)]. This product, which was identified as $[\text{Pd}\{[(\eta^5\text{-C}_5\text{H}_5)\text{-CH=N-(C}_6\text{H}_4\text{-2-SMe)]Fe}(\eta^5\text{-C}_5\text{H}_5)\}\text{Cl}(\text{PPh}_3)]$ (**8b**),

arose from **5b** by cleavage of the Pd–SMe bond and the incorporation of a PPh_3 ligand in the coordination sphere of the palladium(II). The differences observed in the ^{31}P NMR chemical shifts of **6b** and **8b** were consistent with those found for other palladacycles containing $[\text{C}(\text{sp}^2, \text{phenyl}), \text{N}, \text{X}]^-$ and $[\text{C}(\text{sp}^2, \text{phenyl}), \text{N}]^-$ ligands [20,22,34].

The results presented here are in sharp contrast with those reported for $[\text{Pd}\{[(\eta^5\text{-C}_5\text{H}_5)\text{-CH=N-(CH}_2\text{)}_3\text{-NMe}_2]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}\text{Cl}]$ which in the presence of PPh_3 gave $[\text{Pd}\{[(\eta^5\text{-C}_5\text{H}_5)\text{-CH=N-(CH}_2\text{)}_3\text{-NMe}_2]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}\text{Cl}(\text{PPh}_3)]$ [Scheme 3(c)] in which the ligand acts as a $[\text{C}(\text{sp}^2, \text{ferrocene}), \text{N}]^-$ bidentate group. In this case the formation of the ionic palladacycle $[\text{Pd}\{[(\eta^5\text{-C}_5\text{H}_5)\text{-CH=N-(CH}_2\text{)}_3\text{-NMe}_2]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}(\text{PPh}_3)]^+$ could

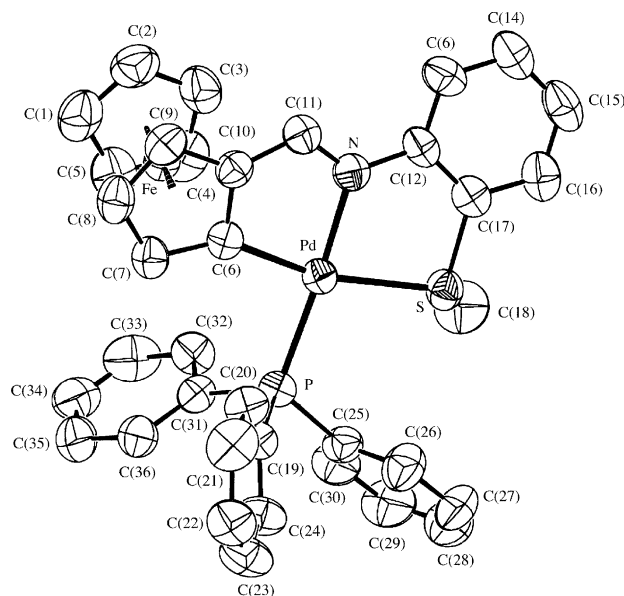


Fig. 4. Molecular structure and atom numbering scheme of the cationic array of: $[\text{Pd}\{[(\eta^5\text{-C}_5\text{H}_5)\text{-CH=N-(C}_6\text{H}_4\text{-2SMe)]Fe}(\eta^5\text{-C}_5\text{H}_5)\}(\text{PPh}_3)]\text{[BF}_4\text{]CH}_2\text{Cl}_2$ (**7b**). Hydrogen atoms are not shown for clarity. [Selected bond lengths (Å) and angles (°): Pd–C(6), 2.001(3); Pd–N, 2.070(2); Pd–P, 2.2506(7); Pd–S, 2.3750(8); C(6)–C(10), 1.451(4); C(10)–C(11), 1.419(4); C(10)–N, 1.313(4); N–C(12), 1.406(3); C(6)–Pd–N, 81.75(10); C(6)–Pd–P, 93.62(8); N–Pd–S, 82.48(7); P–Pd–S, 101.85(3); C(6)–C(10)–C(11), 117.1(2); C(9)–C(10)–C(11), 132.5(3); C(10)–C(11)–N, 116.3(2); Pd–S–C(17), 95.58(10); Pd–S–C(18), 112.62(17) and C(17)–S–C(18), 120.86(18)].

only be achieved in the presence of $\text{Ti}[\text{BF}_4]$. These findings suggested that the Pd–Cl and Pd–X (X = S or N') bonds are more labile in $[\text{Pd}\{[(\eta^5\text{-C}_5\text{H}_5)\text{-CH=N-(CH}_2\text{)}_3\text{-NMe}_2]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}\text{Cl}]$ than in **5b**.

In a first attempt to explain the different stability of the ionic cyclopalladated complexes holding a $[\text{C}(\text{sp}^2, \text{ferrocene}), \text{N}, \text{X}]^+$ terdentate ligands **7b** and $[\text{Pd}\{[(\eta^5\text{-C}_5\text{H}_5)\text{-CH=N-(CH}_2\text{)}_3\text{-NMe}_2]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}(\text{PPh}_3)]\text{[BF}_4\text{]}\cdot\text{CHCl}_3$ (**9b**) [23b], we decided to crystallise **9b** and to solve its crystal structure. The structure consists of equimolar amounts of heterodimetallic cations: $[\text{Pd}\{[(\eta^5\text{-C}_5\text{H}_5)\text{-CH=N-(CH}_2\text{)}_3\text{-NMe}_2]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}(\text{PPh}_3)]^+$, $[\text{BF}_4]^-$ anions and CHCl_3 . The molecular structure of the cationic array is shown in Fig. 5.

The palladium(II) atom is bound to the N(1) and N(2) atoms of the ligand, the C(6) atom of the ferrocenyl group and the phosphorous atom of the PPh_3 ligand in a slightly distorted square-planar environment. The Pd–N(2) and Pd–C(6) bond lengths do not differ significantly from those reported for $[\text{Pd}\{[(\eta^5\text{-C}_5\text{H}_5)\text{-CH=N-(CH}_2\text{)}_3\text{-NMe}_2]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}\text{Cl}]$ (**1b**) [Pd–N(2), 2.205(3) Å and Pd–C(6), 1.964(3) Å] (the differences do not clearly exceed 3σ), but the Pd–N(1) bond in **9b** is larger than in **1b**.

The metallacycle has an envelope-like conformation in which the C(6) atom deviates by ca. 0.198 Å [towards the Fe(II) ion] from the main plane defined by the re-

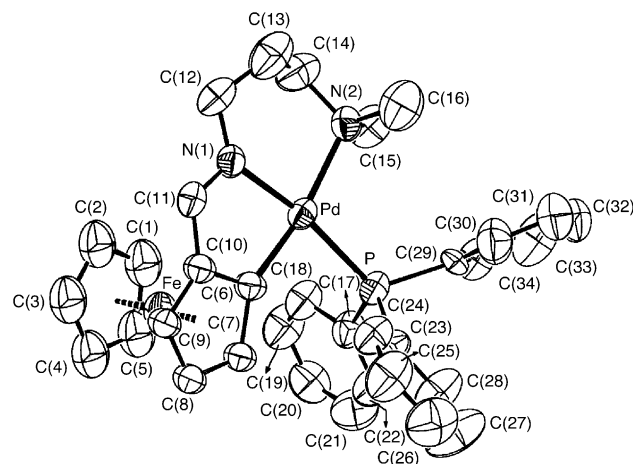
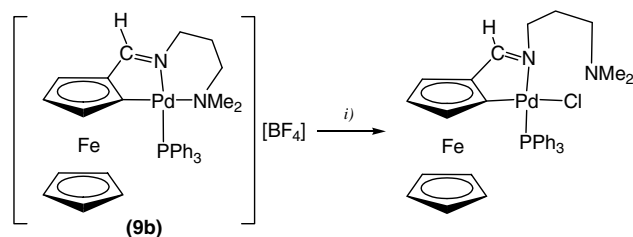


Fig. 5. Molecular structure and atom numbering scheme of the cationic array of: $[\text{Pd}\{[(\eta^5\text{-C}_5\text{H}_5)\text{-CH=N-(CH}_2\text{-CH}_2\text{-CH}_2\text{-NMe}_2)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}(\text{PPh}_3)]\text{[BF}_4\text{]}\cdot\text{CHCl}_3$ (**9b**). Hydrogen atoms are not shown for clarity. [Selected bond lengths (Å) and angles (°): Pd–C(6), 1.946(11); Pd–N(1), 2.125(4); Pd–N(2), 2.195(8); Pd–P, 2.2841(9); C(6)–C(10), 1.482(8); C(10)–C(11), 1.456(12); C(11)–N(1), 1.290(11); N(1)–C(12), 1.395(10); C(12)–C(13), 1.488(13); C(13)–C(14), 1.459(8); C(14)–N(2), 1.505(6); C(6)–Pd–N(1), 82.7(3); N(1)–Pd–N(2), 89.2(3); N(2)–Pd–P, 103.07(10); C(6)–Pd–P, 85.69(13), C(11)–N(1)–C(12), 116.1(6)].

maining atoms. The six-membered ring formed by the coordination of the two nitrogen atoms {N(1) and N(2)} to the palladium has a half-chair conformation.

The pentagonal rings of the ferrocenyl fragment are planar, nearly parallel (*tilt angle* = 4.0°) and they deviate by ca. -6.9° from the ideal eclipsed conformation.

The comparison of structural data for compounds **7b** and **9b** reveal that the sum of the bond angles around the palladium involving the phosphorous atom: C(6)–Pd–P and P–Pd–N(2) (in **9b**) or P–Pd–S (in **7b**) [195.5°] is greater than in **9b** [188.8°]. These findings together with the shorter the Pd–N(2) bond (in **9b**) when compared with the Pd–S bond distance (in **7b**) indicate that the environment of the PPh_3 in **9b** is more constrained than in **7b**. In fact, when **9b** is treated with the equimolar amount of LiCl in a $\text{CH}_2\text{Cl}_2\text{:MeOH}$ (10:1 mixture) at ca. 20°C , the Pd–N(amine) bond cleaves, producing $[\text{Pd}\{[(\eta^5\text{-C}_5\text{H}_5)\text{-CH=N-(CH}_2\text{)}_3\text{-NMe}_2]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}\text{Cl}(\text{PPh}_3)]$ (Scheme 5); while for **7b** more severe experimental conditions were needed to cleave the Pd–S bond. These



Scheme 5. (i) LiCl in a $\text{CH}_2\text{Cl}_2\text{:MeOH}$ (10:1) mixture at room temperature for 5 min.

findings agree with the different hardness [19] of the two heteroatoms N_{amine} (in **9b**) and S (in **7b**).

3. Conclusions

The results presented in this work have allowed us to elucidate the relative importance of the metallated carbon atom and/or the nature of the terminal X donor atom of the [C,N,X][−] terdentate ligands in pallada- and platinacycles of general formulae [M(C,N,X)Cl] upon the reactivity of the M–X bond and the M–Cl bond. In particular, these studies reveal that: (a) the Pt–Cl bond (in **5a**) is more labile than in **5b** and (b) compounds **5a**, **5b** are less proclive to undergo a ring opening process than **3–4a,b**, which contain a [C(sp², phenyl), N,S][−] ligand [25,26].

On the other hand, the variations detected in the M–L bond length within a family of related compound has been frequently used to rationalise the different reactivity of the complexes towards a given ligand. Commonly, larger σ(M–L) bond distances are related to the greater lability of the bond. The differences observed in the M–C, M–N and M–Cl bond distances in **4a** and **5a** (or in **4b** and **5b**) (Table 1) do not clearly exceed 3σ; but in **4a** and **4b** the M–S bond lengths are clearly larger than in **5a** and **5b**. This finding could be indicative of a weaker M–S bond in the metallated complexes with a [C(sp², phenyl), N,S][−] terdentate ligand, which is consistent with the results obtained from the experimental work presented here.

4. Experimental

4.1. Materials and methods

Compounds [M{[(η⁵-C₅H₅)-CH=N-(C₆H₄-2-SMe)]Fe(η⁵-C₅H₅)}Cl] [with M = Pt (**5a**) or Pd (**5b**)], [Pt{[(η⁵-C₅H₅)-CH=N-(CH₂)₃-NMe₂]}Fe(η⁵-C₅H₅)}(PPh₃)] [BF₄] (**9b**) and Ti[BF₄] were prepared as described previ-

ously [23a,28,35]. The solvents (except benzene) were dried and distilled before use [36]. Some of the preparations described below require the use of *HIGHLY HAZARDOUS* materials such Ti[BF₄] or benzene, which should be handled with *CAUTION*.

Elemental analyses (C, H, N and S) were carried out at the Serveis de Recursos Científics i Tècnics (University of Rovira i Virgili, Tarragona). FAB⁺ mass spectra were performed at the Servei d'Espectrometria de Masses (University of Barcelona) using 3-nitrobenzylalcohol (NBA) as matrix.

Infrared spectra were obtained with a Nicolet 400-FTIR instrument using KBr pellets. Routine ¹H and ¹³C{¹H} NMR spectra were obtained with a Gemini 200 MHz and a Bruker 250-DXR or a Mercury 400 MHz instruments, respectively. High-resolution ¹H NMR spectra and the two dimensional [{¹H–¹H}] NOESY, ROESY and COSY and {¹H–¹³C}-heteronuclear single quantum coherence (HSQC) and the heteronuclear multiple bond coherence (HMBC) NMR experiments were recorded with either a Varian VRX-500 or with a Bruker Advance DMX 500 instruments at 20 °C. Variable temperature ¹H- and ³¹P{¹H} NMR spectra were carried out using a Bruker Advance DMX 500 and a Bruker 250-DXR instruments, respectively. In all the NMR experiments the solvent was CDCl₃ (99.8%) and SiMe₄ was used as internal reference. ³¹P{¹H} and ¹⁹⁵Pt{¹H} NMR spectra (at 20 °C) were obtained with a Bruker 250-DXR instruments in CDCl₃ (99.9%) and using P(O)Me₃ [δ ³¹P = 141.1 ppm] and H₂[PtCl₆] [δ ¹⁹⁵Pt = 0.0 ppm] as references, respectively.

4.2. Preparation of the compounds

4.2.1. Preparation of [Pt{[(η⁵-C₅H₅)-CH=N-(C₆H₄-2-SMe)]Fe(η⁵-C₅H₅)}Cl] [Fe(η⁵-C₅H₅)}(PPh₃)]Cl (**6a**)

Compound [Pt{[(η⁵-C₅H₅)-CH=N-(C₆H₄-2-SMe)]Fe(η⁵-C₅H₅)}Cl] (**5a**) (61 mg, 1.08 × 10^{−4} mol) was dissolved in 10 ml of CH₂Cl₂, then the stoichiometric amount of PPh₃ was added. The reaction

Table 1

Selected bond lengths (Å) and angles (°) for the cyclopalladated complexes of general formulae: [M{[(C₆H₄)-CH=N-(C₆H₄-2-SMe)]Fe(η⁵-C₅H₅)}Cl] {M = Pt (**4a**), Pd (**4b**)} and [M{[(η⁵-C₅H₅)-CH=N-(C₆H₄-2-SMe)]Fe(η⁵-C₅H₅)}Cl] {M = Pt (**5a**), Pd (**5b**)} (standard deviation parameters are given in parenthesis)^a

	M = Pt		M = Pd	
	4a	5a	4b	5b
M–S	2.349(2)	2.328(3)	2.3863(13)	2.3653(11)
M–C(6)	2.016(6)	1.985(10)	1.987(3)	1.978(5)
M–N	1.988(6)	1.998(7)	2.008(3)	2.020(3)
M–Cl	2.292(2)	2.302(4)	2.3006(17)	2.2851(11)
C(6)–M–N	81.8(2)	80.8(4)	81.94(10)	81.38(16)
N–M–S	85.93(15)	85.6(2)	84.83(9)	84.72(8)
C(6)–M–Cl	96.7(2)	96.3(4)	96.46(10)	95.52(15)
Cl–M–S	95.69(9)	97.60(13)	96.90(5)	98.83(6)

^a Data from [24b,26,28].

mixture was stirred at room temperature (ca. 20 °C) for 1 h and then filtered out. The filtrate was then concentrated to dryness on a rotary evaporator and the purple solid obtained was then washed several times with small portions of *n*-hexane. The purple solid was air-dried and then dried in vacuum for 4 days (yield: 61 mg, 68.5%). Characterisation data: Anal. (%). Calc. for $C_{36}H_{31}NClFeSPPt$ (found): C, 52.28(52.6); H, 3.78(4.1); N, 1.69(1.8) and S, 3.88(4.11). MS (FAB⁺): $m/z = 792$ $\{[M-Cl]^+\}$. IR: 1533 cm^{-1} [$\nu(C=N-)$]. ¹H NMR data (500 MHz): at 300 K, δ (in ppm) = 2.00 (br., 3H, SMe), 3.75 (s, 1H, H³), 4.20 (br., 5H, C₅H₅), 4.73 (s, 1H, H⁴), 5.09 (s, 1H, H⁵), 7.30 (t, 1H, H^{3'}, $J = 8$), 7.34 (d, 1H, H^{3'}, $J = 8$), 7.47 (t, 1H, H^{4'}, $J = 8$), 7.50–7.70 (m, 15 H, aromatic protons of PPh₃), 8.15 (d, 1H, H^α proton of one of the phenyl rings of the PPh₃, $J = 8.0$) and 9.61 (d, 1H, $-CH=N-$, $^4J_{P-H} = 9.0$); at 230 K (major component): δ (in ppm) = 2.13 (br., 3H, SMe), 3.72 (s, 1H, H³), 4.00 (br., 5H, C₅H₅), 4.72 (s, 1H, H⁴), 5.02 (s, 1H, H⁵), 7.31 (t, 1H, H^{4'}, $J = 7.9$), 7.36 (d, 1H, H^{3'}, $J = 7.9$), 7.44 (t, 1H, H^{5'}, $J = 7.9$), 7.50–7.70 (m, 15 H, H^{6'} and 14 aromatic protons of PPh₃), 8.04 (d, 1H, H^α of one of the phenyl rings of the PPh₃ group, $J = 8$) and 9.51 (d, 1H, $-CH=N-$, $^3J_{Pt-H} = 100$, $^4J_{P-H} = 9$); (minor component): δ (in ppm) = 1.82 (br., 3H, SMe), 3.72 (s, 1H, H³), 4.39 (br., 5H, C₅H₅), 4.72 (s, 1H, H⁴), 5.08 (s, 1H, H⁵), 7.29 (t, 1H, H^{4'}, $J = 8$), 7.45 (t, 1H, H^{5'}, $J = 8$), 7.50–7.70 (m, 15 H, H^{6'} and 14 aromatic protons of PPh₃), 8.11 (H^α of one of the phenyl rings of the PPh₃ group, $J = 8.5$) and 9.60 (d, 1H, $-CH=N-$, $^3J_{Pt-H} = 100$, $^4J_{P-H} = 9$) in this case the resonances due to the H³ and H^{4'} were partially overlapped and masked, respectively, by the signals due to the same protons of the major component. ¹³C{¹H} NMR data (100.58 MHz): at 300 K, δ (in ppm) = 27.9 (SMe), 71.2 (C⁵), 72.0 (C₅H₅), 72.4 (C⁴), 75.8 (C³), 80.1 [C¹, $J_{Pt-C} = 121.8$], 92.7 (C², $J_{Pt-C} = 56$), 120.3 (C^{3'}, $J_{Pt-C} = 55.8$), 128.4 (C^{2'}), 129.1 (C^{4'}), 129.9 (C^{6'}), 143.5 (C^{1'}), 172.6 ($-CH=N-$) and four additional doublets due to the four types of carbon-13 nuclei of the PPh₃ at 129.5, 132.2, 133.2 and 134.4. ³¹P{¹H} NMR data: at 300 K, δ (in ppm) = 15.2 ($^1J_{Pt-P} = 3785$); at 230 K, δ (in ppm) = 15.5 ($^1J_{Pt-P} = 3763$) and 15.20 ($^1J_{Pt-P} = 3763$). ¹⁹⁵Pt{¹H} NMR data at 300 K, δ (in ppm) = -4449 ($^1J_{Pt-P} = 3785$).

4.2.2. Preparation of $[Pd\{[(\eta^5-C_5H_5)-CH=N-(C_6H_4-2-SMe)]Fe(\eta^5-C_5H_5)\}Fe(\eta^5-C_5H_5)\}(PPh_3)]Cl$ (**6b**)

To a solution containing (43 mg, 9.04×10^{-5} mol) of $[Pd\{[(\eta^5-C_5H_5)-CH=N-(C_6H_4-2-SMe)]Fe(\eta^5-C_5H_5)\}Fe(\eta^5-C_5H_5)]Cl$ (**5b**) and 20 ml of acetone, triphenylphosphine (35 mg, 1.34×10^{-4} mol) was added. The reaction mixture was refluxed for 2 h. After this period the resulting deep purple solution was filtered out and the filtrate was concentrated to dryness on a rotary evaporator. The residue was dissolved in the minimum amount

of CH₂Cl₂ and passed through a short (2.5 cm × 3.0 cm) SiO₂ column chromatography. Elution with a CH₂Cl₂:MeOH (100:4) produced the release of a deep-purple band which was collected and concentrated to dryness. The solid isolated (**6b**) was collected and dried in vacuum for 3 days (yield: 50 mg, 72.8%). Characterisation data: Anal. (%) Calc. for $C_{36}H_{31}NClFeSPPd \cdot 1/4 CH_2Cl_2$ (found): C, 57.31(57.4); H, 4.11(4.2); N, 1.85(1.8) and S, 4.37(4.2). MS (FAB⁺): $m/z = 703$ $[M - 1/4(CH_2Cl_2) - Cl]^+$. IR: 1544 cm^{-1} [$\nu(C=N-)$]. ¹H NMR data (500 MHz): δ (in ppm) = 1.99 (s, 3H, SMe), 3.77 (d, 1H, H³, $J = 2$), 4.24 (s, 5H, C₅H₅), 4.57 (t, 1H, H⁴, $J = 2$), 5.07 (d, 1H, H⁵, $J = 2$), 5.12 (s, 0.5H, CH₂Cl₂), 8.50 (d, 1H, H^{3'}, $J = 7.5$), 7.30 (t, 1H, H^{4'}, $J = 7.5$), 7.55 (t, 1H, H^{5'}, $J = 7.5$), 7.37 (d, 1H, H^{6'}, $J = 7.5$), 7.50–7.82 (m, 15H, aromatic protons of PPh₃) and 9.47 (s, 1H, $-CH=N-$, $^4J_{P-H} = 8.5$ Hz). ¹³C{¹H} NMR (100.5 MHz): δ (in ppm) = 24.8 (SMe), 71.7 (C₅H₅), 79.2 (d, C³, $J_{P-C} = 6.6$ Hz), 73.0 (C⁴), 71.4 (C⁵), 91.5 (C¹), 108.5 (d, C², $J_{P-C} = 8.4$), 128.2 (C^{2'}), 119.5 (C^{3'}), 128.4 (C^{4'}), 132.2 (C^{5'}), 133.6 (C^{6'}), 148.7 (C^{1'}), 171.5 ($\nu(C=N-)$) and four additional doublets centered at 128.5, 130.5, 131.4 and 134.0 ppm due to the four types of carbon-13 nuclei of the phenyl rings of the PPh₃. ³¹P{¹H} NMR: δ (in ppm) = 34.8.

4.2.3. Preparation of $[Pt\{[(\eta^5-C_5H_5)-CH=N-(C_6H_4-2-SMe)]Fe(\eta^5-C_5H_5)\}Fe(\eta^5-C_5H_5)\}(PPh_3)] [BF_4]$ (**7a**)

To a solution containing 44 mg (5.3×10^{-5} mol) of $[Pt\{[(\eta^5-C_5H_5)-CH=N-(C_6H_4-2-SMe)]Fe(\eta^5-C_5H_5)] [Fe(\eta^5-C_5H_5)]Cl$ (**5a**) and 10 ml of acetone, Tl[BF₄] (23 mg, 7.9×10^{-5} mol) was added. The reaction mixture was stirred at ca. 20 °C for 1 h and then filtered. The filtrate was concentrated to dryness on a rotary evaporator and then treated with the minimum amount of CH₂Cl₂. The undissolved materials were removed by filtration and the resulting purple solution was concentrated to dryness on a rotary evaporator giving a deep purple solid (yield: 38 mg, 90.5%). Characterisation data: Anal. (%) Calc. for $C_{36}H_{31}NBF_4FeSPPt \cdot 1/2CH_2Cl_2$ (found): C, 47.61(47.8); H, 3.50(3.80); N, 1.52(1.6) and S, 3.48 (3.1). FAB⁺(MS): $m/z = 792$ $\{M-[BF_4]^- \}$. IR (in cm^{-1}): 1533 [$\nu(C=N-)$] and 1062 [BF₄]⁻. ¹H NMR data (500 MHz): at 300 K, δ (in ppm) = 2.0 (br., 3H, SMe), 3.75 (s, 1H, H³), 4.20 (br., 5H, C₅H₅), 4.73 (s, 1H, H⁴), 5.09 (s, 1H, H⁵), 7.30 (t, 1H, H^{2'}, $J = 8$), 7.34 (d, 1H, H^{3'}), 7.47 (t, 1H, H^{4'}), 7.50–7.70 (m, 15 H, aromatic protons of PPh₃), 8.15 (d, 1H, H^α of one of the phenyl rings of the PPh₃ group, $J = 7.5$) and 9.61 (d, 1H, $-CH=N-$, $^3J = 100$, $^4J_{P-H} = 9$); at 230 K (major component): δ (in ppm) = 2.13 (br., 3H, SMe), 3.72 (s, 1H, H³), 4.00 (br., 5H, C₅H₅), 4.72 (s, 1H, H⁴), 5.02 (s, 1H, H⁵), 7.31 (t, 1H, H^{4'}), 7.36 (d, 1H, H^{3'}), 7.44 (t, 1H, H^{5'}), 7.50–7.70 (m, 15 H, H^{6'} and 14 aromatic protons of PPh₃), 8.04 (d, 1H, H^α of one of the phenyl rings

of the PPh_3 group, $J = 7.5$), 9.51 (d, 1H, $-\text{CH}-\text{N}-$, $^4J_{\text{P-H}} = 9$); (minor component): δ (in ppm) = 1.82 (br., 3H, SMe), 3.72 (s, 1H, H^3), 4.39 (br., 5H, C_5H_5), 4.72 (s, 1H, H^4), 5.08 (s, 1H, H^5), 7.29 (t, 1H, $\text{H}^{4'}$), 7.45 (t, 1H, $\text{H}^{5'}$), 7.50–7.70 (m, 15 H, $\text{H}^{6'}$ and 14 aromatic protons of PPh_3), 8.11 (H_α of one of the phenyl rings of the PPh_3 group, $J = 8.5$), 9.60 (d, 1H, $-\text{CH}-\text{N}-$, $^4J_{\text{P-H}} = 9$), in this case the resonances due to the H^3 and $\text{H}^{4'}$ were partially overlapped or masked, respectively by the signals due to the same protons of the major component. $^{13}\text{C}\{^1\text{H}\}$ NMR data (100.58 MHz): at 300 K, δ (in ppm) = 27.9 (SMe), 71.2 (C^5), 72.0 (C_5H_5), 72.4 (C^4), 75.8 (C^3), 80.1 (C^1 , $J_{\text{Pt-C}} = 121.8$), 92.7 (C^2 , $J_{\text{Pt-C}} = 56$), 120.3 ($\text{C}^{3'}$, $J_{\text{Pt-C}} = 55.8$), 128.4 ($\text{C}^{2'}$), 129.1 ($\text{C}^{4'}$), 129.9 ($\text{C}^{6'}$), 143.5 ($\text{C}^{1'}$), 172.6 ($-\text{CH}=\text{N}-$) and four additional doublets due to the four types of carbon-13 nuclei of the PPh_3 at 129.5, 132.2, 133.2 and 134.4. $^{31}\text{P}\{^1\text{H}\}$ NMR data: at 300 K, δ (in ppm) = 15.2 ($^1J_{\text{Pt-P}} = 3785$); at 230 K, $\delta = 15.5$ ($^1J_{\text{Pt-P}} = 3763$) and 15.20 ($^1J_{\text{Pt-P}} = 3763$). $^{195}\text{Pt}\{^1\text{H}\}$ NMR data at 300 K δ (in ppm) = -4449 ($^1J_{\text{Pt-P}} = 3763$).

4.2.4. Preparation of $[\text{Pd}\{[(\eta^5\text{-C}_5\text{H}_5)\text{-CH}=\text{N}-(\text{C}_6\text{H}_4\text{-SMe})]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}\text{Cl}(\text{PPh}_3)] [\text{BF}_4]$ (**7b**)

This compound was prepared using either compound **5b** or complex **6b** as starting materials [methods (a) and (b), respectively].

Method (a): In this case the synthesis was achieved according to the procedure described above for **7a** but using 5.3×10^{-5} mol of $[\text{Pd}\{[(\eta^5\text{-C}_5\text{H}_5)\text{-CH}=\text{N}-(\text{C}_6\text{H}_4\text{-SMe})]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}\text{Cl}]$ (**5b**) and the stoichiometric amounts of $\text{Ti}[\text{BF}_4]$ and PPh_3 as starting materials. The complex was recrystallised in CH_2Cl_2 (yield: 28 mg, 64%).

Method (b): Compound **6b** (53 mg, 6.98×10^{-5} mol) was dissolved in 20 ml of acetone, then the equimolar amount of $\text{Ti}[\text{BF}_4]$ (20 mg, 6.98×10^{-5}) was added. The reaction mixture was stirred at room temperature for 1 h and then the thallium(I) chloride formed was removed by filtration and discarded. The filtrate was concentrated to dryness on a rotary evaporator. The deep residue was dissolved in the minimum amount of CH_2Cl_2 (ca. 5 ml) and the undissolved materials were removed by filtration. The filtrate was concentrated to dryness on a rotary evaporator and the solid formed was dried in vacuum for 2 days (yield: 40 mg, 77%).

4.2.4.1. Characterisation data. Anal. (%) Calc. for $\text{C}_{36}\text{H}_{31}\text{NBF}_4\text{FeSPPd} \cdot \text{CH}_2\text{Cl}_2$ (found): C, 50.81(50.4), H, 3.80(3.8), N, 1.60(1.60) and S, 3.66(3.3). MS(FAB⁺): $m/z = 703$ $[\text{M}-[\text{BF}_4]^-]$. IR (in cm^{-1}): 1544 [$\nu(\text{C}=\text{N})$]; 1096 $[\text{BF}_4]^-$. ^1H NMR data (500 MHz): δ (in ppm) = 1.99 (s, 3H, SMe), 3.77 (d, 1H, H^3 , $J = 2$), 4.24 (s, 5H, C_5H_5), 4.57 (t, 1H, H^4 , $^3J = 2$), 5.07 (d, 1H,

H^5 , $J = 2$), 7.30 (t, 1H, $\text{H}^{4'}$, $J = 7.5$); 7.37 (d, 1H, $\text{H}^{6'}$, $J = 7.5$), 7.55 (t, 1H, $\text{H}^{5'}$, $^3J = 7.5$); 7.50–7.82 (m, 15H, aromatic protons of PPh_3) 8.50 (d, 1H, $\text{H}^{3'}$, $^3J = 7.5$), and 9.47 (s, 1H, $-\text{CH}=\text{N}-$, $^4J_{\text{P-H}} = 8.5$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.5 MHz): δ (in ppm) = 24.8(SMe), 71.4 (C^5), 71.7 (C_5H_5), 73.0 (C^4), 79.2 (d, C^3 , $J_{\text{P-C}} = 6.6$), 91.5 (C^1), 108.5 (d, C^2 , $J_{\text{P-C}} = 8.4$), 119.5 ($\text{C}^{3'}$), 128.2 ($\text{C}^{2'}$), 128.4 ($\text{C}^{4'}$), 132.2 ($\text{C}^{5'}$); 133.6 ($\text{C}^{6'}$), 148.7 ($\text{C}^{1'}$), 171.5 ($\text{C}=\text{N}-$) and four additional doublets centered at 128.5, 130.5, 131.4 and 134.0 ppm due to the four types of carbon-13 nuclei of the phenyl rings of the PPh_3 . $^{31}\text{P}\{^1\text{H}\}$ NMR: δ (in ppm) = 34.9.

4.2.5. Preparation of $[\text{Pd}\{[(\eta^5\text{-C}_5\text{H}_5)\text{-CH}=\text{N}-(\text{C}_6\text{H}_5\text{-2SMe})]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}\text{Cl}(\text{PPh}_3)]$ (**8b**)

A mixture containing 51 mg (1.07×10^{-4} mol) of $[\text{Pd}\{[(\eta^5\text{-C}_5\text{H}_5)\text{-CH}=\text{N}-(\text{C}_6\text{H}_5\text{-2SMe})]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}\text{Cl}]$ (**5b**), triphenylphosphine (42 mg, 1.6×10^{-4} mmol) and benzene (10 ml) was refluxed for 24 h. After this period the reaction mixture was allowed to cool to room temperature and then filtered out. The purple solution was concentrated to dryness on a rotary evaporator. The residue was then dissolved in the minimum amount of CH_2Cl_2 and passed through a short SiO_2 column chromatography (2.0 cm \times 2.5 cm). Elution with CH_2Cl_2 produced the release of a purple band which was collected and then concentrated to dryness on a rotary evaporator. The solid obtained was air-dried and then dried in vacuum for 2 days (yield: 69 mg, 87%). Characterisation data: Anal. (%) Calc. for $\text{C}_{36}\text{H}_{31}\text{NClFeSPdP}$ (found): C, 58.6 (58.3); H, 4.23(4.5); N, 1.90(1.8) and S, 4.34(4.2). MS(MALDI-TOF⁺): $m/z = 738$ $[\text{M}]^+$, 702 $[\text{M}-\text{Cl}]^+$, 669 $[\text{M}-\text{Cl}-\text{CH}_3]^+$. IR (in cm^{-1}): 1544 [$\nu(\text{C}=\text{N})$]. ^1H NMR data (500 MHz): δ (in ppm) = 2.37 (s, 3H, SMe); 3.64 (s, 1H, H^3), 3.94 (s, 5H, C_5H_5), 4.39 (s, 1H, H^4), 4.50 (s, 1H, H^5), 6.77 (t, 1H, $\text{H}^{4'}$, $J = 8$), 6.90 (t, 1H, $\text{H}^{5'}$, $J = 8$), 7.22 (d, 1H, $\text{H}^{3'}$, $J = 8$), 7.27 (d, 1H, $\text{H}^{6'}$, $J = 8$), 8.54 (d, 1H, $-\text{CH}=\text{N}-$, $J_{\text{P-H}} = 9$) and 7.55–7.80 (m, 15H, aromatic protons of the PPh_3 ligand). $^{13}\text{C}\{^1\text{H}\}$ NMR data (in ppm): $\delta = 18.12$ (SMe), 68.7 (C^3), 70.8 (C_5H_5), 72.2 (C^4), 79.2 (C^4), 92.6 (C^1), 106.6 (C^2), 114.9 ($\text{C}^{3'}$), 122.2 ($\text{C}^{4'}$), 127.7 ($\text{C}^{5'}$), 131.4 ($\text{C}^{6'}$), 149.5 ($\text{C}^{1'}$), 147.4 ($\text{C}^{2'}$), 163.6 ($\text{C}=\text{N}-$) and three additional doublets centered at: 128.8, 129.2, 131.0 and 134.7 due to the four types of carbon nuclei of the PPh_3 ligand. $^{31}\text{P}\{^1\text{H}\}$ NMR data (in ppm): $\delta = 38.1$.

4.3. Crystallography

A prismatic crystal of **7b** or **9b** (sizes in Table 2) was selected and mounted on a MAR345 diffractometer with a image plate detector. Unit cell parameters were determined from automatic centering of 9390 (for **7b**) or 4616 (for **9b**) reflections in the range $3^\circ < \theta < 31^\circ$, and refined

Table 2

Crystal data and details of the refinement of the crystal structures of $[\text{Pd}\{(\eta^5\text{-C}_5\text{H}_5)\text{-CH=N-(C}_6\text{H}_4\text{-2-SMe)}\}\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}(\text{PPh}_3)]\text{[BF}_4\text{]}\cdot\text{CH}_2\text{Cl}_2$ (**7b**) and $[\text{Pd}\{[(\eta^5\text{-C}_5\text{H}_5)\text{-CH=N-(CH}_2\text{-CH}_2\text{-CH}_2\text{-NMe}_2)]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}(\text{PPh}_3)]\text{[BF}_4\text{]}\cdot\text{CHCl}_3$ (**9b**) (standard deviation parameters are given in parenthesis)

	7b	9b
Empirical formula	$\text{C}_{37}\text{H}_{32}\text{BCl}_2\text{F}_4\text{FeNPPdS}$	$\text{C}_{35}\text{H}_{36}\text{BCl}_3\text{F}_4\text{FeN}_2\text{PPdS}$
Formula weight	838.18	871.04
Crystal size (mm \times mm \times mm)	$0.1 \times 0.1 \times 0.2$	$0.1 \times 0.1 \times 0.2$
<i>T</i> (K)	293(2)	293(2)
λ (Å)	0.71069	0.71069
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
<i>a</i> (Å)	10.6170(10)	10.3190(10)
<i>b</i> (Å)	12.9620(10)	10.6520(10)
<i>c</i> (Å)	13.9270(10)	17.3220(10)
α (°)	82.845(10)	84.40
β (°)	79.589(10)	87.08
γ (°)	74.286(10)	74.14
<i>V</i> (Mg m ^{−3})	1808.8(3)	1822.2(3)
Absorption coefficient (mm ^{−1})	1.122	1.204
<i>F</i> (000)	844	878
θ range for data collection (°)	2.02–31.61	2.36–31.59
Number of collected reflections	12681	3003
Number of unique reflections (<i>R</i> _{int})	8353 (0.0319)	3003 (0.0267)
Number of data	8353	3003
Number of parameters	442	434
Goodness-of-fit on <i>F</i> ²	1.048	1.075
<i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0413, <i>wR</i> ₂ = 0.1202	<i>R</i> ₁ = 0.0331, <i>wR</i> ₂ = 0.0953
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0604, <i>wR</i> ₂ = 0.1296	<i>R</i> ₁ = 0.0401, <i>wR</i> ₂ = 0.0987
Largest difference in peak and hole (e Å ^{−3})	0.809 and −0.843	0.251 and −0.360

by full-matrix least-squares method. Intensities were collected with graphite monochromatized Mo-K α radiation. For **7b**, the number of measured reflections was 12681 (in the range $2.02^\circ \leq \theta \leq 31.61^\circ$) and for **9b**, 3003 reflections were measured in the range $2.36^\circ \leq \theta \leq 31.59^\circ$. The number of reflections assumed as observed applying the condition $I > 2\sigma(I)$ was 8353 (for **7b**) and 2626 (for **9b**). Lorentz-polarisation corrections were made, but absorption corrections were not.

The structures were solved by Direct methods, using SHELXS computer program [37] and refined by full-matrix least-squares method with the SHELX-97 computer program [38] using 8353 reflections (very negative reflections were not assumed). The function minimised was $\sum w = \|F_o\|^2 - |F_c|^2$, where $w = [\sigma^2(I) + (0.0909P)^2]^{-1}$ (for **7b**) and $w = [\sigma^2(I) + (0.0688P)^2] + (0.3904P)^{-1}$ and $P = (|F_o|^2 + 2|F_c|^2)/3$; *f*, *f'* and *f''* were obtained from the literature [39]. For **7b**, the fluorine atoms of the $[\text{BF}_4]^-$ anion were located in disordered positions. An occupancy factor equal to 0.5 was assumed according to the height of the difference synthesis. For the two structures, all hydrogen atoms were computed and refined using a riding model with an isotropic temperature factor equal to 1.2 times the equivalent temperature factor of the atom linked to it. The final *R* (on *F*) factor was 0.041, *wR* (on *F*_o) = 0.120. Further details concerning the resolution and refinement of the crystal structures are presented in Table 2.

Acknowledgements

This work was performed with the financial support of the Ministerio de Ciencia y Tecnología of Spain, the Generalitat de Catalunya (Grant Nos. BQU2003-00906 and SRG2001-00054, respectively) and FEDER funds. S.P. is grateful to the Generalitat de Catalunya for a pre-doctoral fellowship.

Appendix A. Supplementary material

Crystallographic data for the structural analyses of **7b** and **9b** have been deposited at the Cambridge Crystallographic Data Centre, CCDC Nos. 240806 and 240807, respectively. Copies of this information can be obtained from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1233-336033; e-mail: deposit@ccdc.ac.uk or www: <http://www.ccdc.cam.ac.uk>). Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.jorganchem.2004.07.007.

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