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Study of the reactivity of palladacycles containing $[C(sp^2, \text{ferrocene}),N,S]^-$ or $[C(sp^3),N,S]^-$ terdentate ligands with symmetric alkynes

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Abstract

The study of the reactivity of the cyclopalladated complex $[Pd\{[(\eta^5\text{-}C_5H_3)\text{–}CH{=}N\text{–}(C_6H_4\text{–}2\text{-}SMe)]Fe(\eta^5\text{-}C_5H_5)\}Cl]$ (**1c**) with the alkynes $R^1\text{–}C{\equiv}C\text{–}R^1$ (with $R^1 = CO_2Me$, Ph or Et) is reported.Compound **1c** reacts with the equimolar amount of $MeO_2C\text{–}C{\equiv}C\text{–}CO_2Me$ in refluxing CH_2Cl_2 to give $[Pd\{[(MeO_2C\text{–}C{=}C\text{–}CO_2Me)(\eta^5\text{-}C_5H_3)\text{–}CH{=}N\text{–}(C_6H_4\text{–}2\text{-}SMe)]Fe(\eta^5\text{-}C_5H_5)\}Cl]$ (**2c**), which arises from the monoinsertion of the alkyne into the σ[Pd–C(sp^2, ferrocene)] bond. However, when the reaction was performed using $Ph\text{–}C{\equiv}C\text{–}Ph$ or $Et\text{–}C{\equiv}C\text{–}Et$ no evidence of the insertion of these alkynes into the σ[Pd–C(sp^2, ferrocene)] bond was detected.In contrast with these results, when **1c** was treated with the $Tl[BF_4]$ followed by the removal of the TlCl formed and the subsequent addition of $MeO_2C\text{–}C{\equiv}C\text{–}CO_2Me$ the reaction gave **2c** and $[Pd\{[(MeO_2C\text{–}C{=}C\text{–}CO_2Me)_2(\eta^5\text{-}C_5H_3)\text{–}CH{=}N\text{–}(C_6H_4\text{–}2\text{-}SMe)]\text{-}Fe(\eta^5\text{-}C_5H_5)\}][BF_4]$ (**3c**); but when the alkyne was $R^1\text{–}C{\equiv}C\text{–}R^1$ (with R^1 = Ph or Et), the ionic palladacycles $[Pd\{[(R^1\text{–}C{=}C\text{–}R^1)_2(\eta^5\text{-}C_5H_3)\text{–}CH{=}N\text{–}(C_6H_4\text{–}2\text{-}SMe)]Fe(\eta^5\text{-}C_5H_5)\}][BF_4]\cdot CH_2Cl_2$ [with R^1 = Ph (**5c**) or Et (**6c**)] were isolated. In compounds **3c**, **5c** and **6c**, the mode of binding of the butadienyl unit is η^3. The reactions of **2c**, **3c**, **5c** and **6c** with PPh_3 are also reported. The results obtained from these studies reveal that the σ(Pd–S) bond in **2c** is more prone to cleave than in **4c**–**6c**. X-ray crystal structures of **2c**, **5c** and $[Pd\{[(MeO_2C\text{–}C{=}C\text{–}CO_2Me)(\eta^5\text{-}C_5H_3)\text{–}CH{=}N\text{–}(C_6H_4\text{–}2\text{-}SMe)]Fe(\eta^5\text{-}C_5H_5)\}Cl(PPh_3)]$ (**7c**), are also described. Compound **7c** arises from **2c** by cleavage of the Pd–S bond and the incorporation of a PPh_3 in the coordination sphere of the palladium. A parallel study focused on the reactions of $[Pd\{[2\text{-}CH_2\text{–}4,6\text{-}Me_2\text{–}C_6H_2]\text{–}CH{=}N\text{–}(C_6H_4\text{–}2\text{-}SMe)\}Cl]$ (**1d**) (with a $[Csp^3,N,S]^-$ terdentate group) with the three alkynes reveals that the σPd–C(sp^2, ferrocene)] bond of **1c** is more reactive than the σ[Pd–C(sp^3)] bond of **1d**.

Keywords: Alkyne insertions; Palladacycles; Ferrocene

1. Introduction

An important area of organometallic chemistry is that focused on cyclopalladated complexes [1]. Interest in such compounds has increased exponentially due to either their physical and/or chemical properties or their potential applications in a wide variety of areas [2–12]. Some examples showing the utility of compounds of this kind in homogeneous catalysis [2a,4], as building blocks for the synthesis of macromolecules [5], for the determination of enantiomeric excesses of chiral reagents or even as chiral recognition agents have been described [6,7]. Besides that, it is well known that palladacycles are useful precursors in the synthesis of organic or organometallic compounds [10–12]. Most of these reactions involve the insertions of small molecules, i.e. alkynes, alkenes, CO or isonitriles into the σ(Pd–C) bond.

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Previous studies on this field have shown that the nature of the final product formed by the insertion of alkynes depends on a wide variety of factors including the nature of the metallated carbon, the electron-withdrawing/electron–donor nature of the substituents on the alkyne, the stoichiometry of the reaction, the remaining ligands bound to the palladium, etc. [10].

Despite the wide variety of cyclopalladated complexes containing a $[C(sp^2, aryl),N,X]^-$ or $[C(sp^3),N,X]^-$ (X = N′, S, or O) terdentate group reported so far [13–15], related derivatives with a σ[Pd–C(sp^2, ferrocene)] bond are not so common [16–18]. Most of the articles published so far refer to compounds [Pd{[(η^5-C_5H_3)–CH=N–$(CH_2)_n$–CH_2–NMe_2]Fe(η^5-C_5H_5)}Cl] [with n = 1 **(1a)** or 2 **(1b)**] [16] (Chart 1). We have recently reported the syntheses and characterisation of [Pd{[(η^5-C_5H_3)–CH=N–(C_6H_4-2-SMe)]Fe(η^5-C_5H_5)}Cl] (**1c**) (Chart 1), which contains a $[C(sp^2, ferrocene),N,S]^-$ terdentate ligand [18].

However, articles focused on the reactivity of the σ[Pd–C(sp^2, ferrocene)] bond of palladacycles holding a $[C(sp^2, ferrocene),N,X]^-$ terdentate ligand are practically restricted to reactions of **1a** and **1b** with the internal alkynes: R^1–C≡C–R^1 (with R^1 = CO_2Me, Ph or Et) [19]. In the view of these facts, we were prompted to study the reactivity of the σ[Pd–C(sp^2, ferrocene)] bond of **1c** and the σ[Pd–C(sp^3)] bond of [Pd(2-CH_2–4,6-Me_2–C_6H_2)–CH=N–(C_6H_4–2-SMe)]Cl] (**1d**) (Chart 1) [14e] versus the alkynes: R^1–C≡C–R^1 (with R^1 = CO_2Me, Ph or Et). This type of study could be useful to elucidate the relative influence of: (a) the type of metallated carbon [C(sp^2, ferrocene) (in **1c**) or C(sp^3) (in **1d**)], (b) the substituents on the alkyne (their electron-donor/electron-withdrawing nature or bulk [20]). The comparison of the results obtained from these studies and those reported recently for **1a** and **1b** [19], may also allow to clarify the relevancy of the electronic properties of the terminal X group of the $[C,N,X]^-$ [X = N′ (in **1a** and **1b**) or S (in **1c** and **1d**)] terdentate ligands upon the lability of the σ(Pd–C) bond and the nature of the final product.

2. Results and discussion

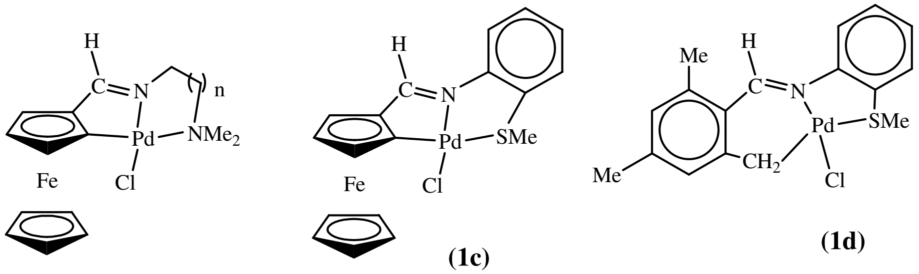
2.1. Insertion of the alkynes into the σ[Pd–C(sp^2, ferrocene)] bond

In a first attempt to study the reactivity of **1c** with the alkynes R^1–C≡C–R^1 (with R^1 = CO_2Me, Ph or Et), we decided to use the most common procedure described in the literature for mono-, bis- or tris-insertions of alkynes, into the σ(Pd–C) bond, which consists on the treatment of mono- or dimeric cyclopalladated complexes with the alkynes (in a alkyne: Pd(II) molar ratio = 1, 2 or 3) in refluxing CH_2Cl_2 or $CHCl_3$ [10,12,19].

The treatment of **1c** with the equimolar amount of MeO_2C–C≡C–CO_2Me in refluxing CH_2Cl_2 for 2 h lead after work up a deep red solid which was identified (see Section 3) as [Pd{[(MeO_2C–C=C–CO_2Me)(η^5-C_5H_3)–CH=N–(C_6H_4-2-SMe)]Fe(η^5-C_5H_5)}Cl] (**2c**) (Scheme 1) which arises from the insertion of one molecule of the alkyne into the σ[Pd–C(sp^2, ferrocene)] bond.

The molecular structure of **2c** (Fig. 1) consists of discrete molecules of [Pd{[(MeO_2C–C=C–CO_2Me)(η^5-C_5H_3)–CH=N–(C_6H_4–2-SMe)]Fe(η^5-C_5H_5)}Cl] separated by van der Waals distances. In each molecule, the palladium(II) is bound to the chlorine, the two heteroatoms (N and S) of the ligand and the terminal carbon of the alkene [C(19)] in a highly distorted square-planar environment [21]. The Pd–N and Pd–C(19) bond lengths [2.030(8) and 1.985(5) Å] do not differ substantially from those reported for **1c** [2.020(3) and 1.978(5) Å, respectively] [18], but the Pd–Cl and Pd–S bond lengths [2.318(5) and 2.390(6) Å] are longer than in **1c** [2.2851(14) and 2.3652(11) Å]. The N–Pd–S and Cl–Pd–S bond angles in **2c** [82.55(12)° and 94.23(12)°, respectively] are smaller than in **1c** [N–Pd–S: 84.72(8)° and Cl–Pd–S: 98.83(6)°] [18]. This may be related to the larger bulk of the $(C,N)^-$ moiety of the chelating group in **2c** when compared with that of **1c**.

The molecule contains a [5,7,5,6] tetracyclic system which arises from the fusion of the 1,2-disubstituted pentagonal ring of the ferrocenyl moiety, a seven-membered

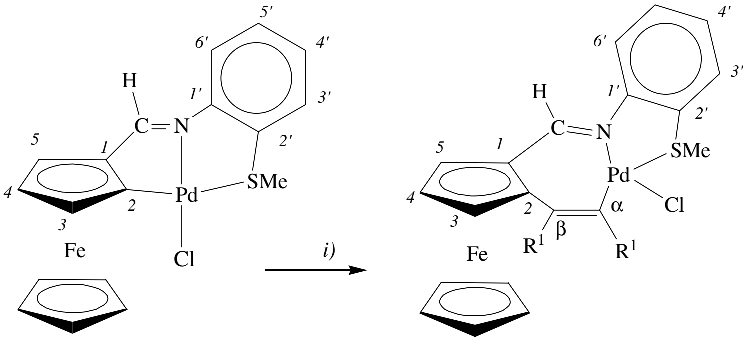


(**1c**)

(**1d**)

n = 1 **(1a)** or 2 **(1b)**

Chart 1.



(1c)

$R^1 = CO_2Me$ (2c)

Scheme 1. (i) Equimolar amount of the alkyne in refluxing CH_2Cl_2,

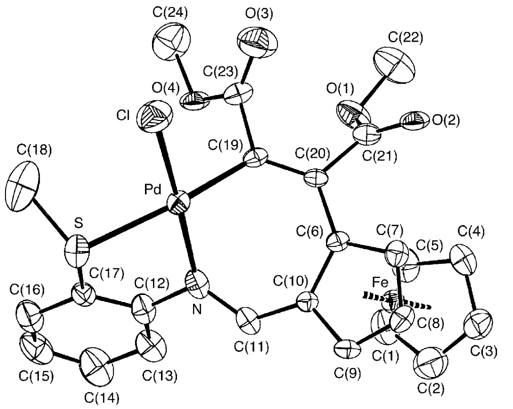


Fig. 1. Molecular structure and atom labelling scheme for [Pd{[(MeO_2C–C=C–CO_2Me)(η^5-C_5H_3)–CH=N–(C_6H_4-2-SMe)]Fe(η^5-C_5H_5)}Cl] (**2c**). Hydrogen atoms have been omitted for clarity. [Selected bond lengths (in Å) and angles (in °): Pd–N, 2.030(8); Pd–S, 2.390(6); Pd–Cl, 2.318(5); Pd–C(19), 1.985(7); C(10)–C(11), 1.452(5); C(11)–N, 1.323(7); S–C(17), 1.759(6); S–C(18), 1.827(9); C(6)–C(20), 1.483(8); C(19)–C(20), 1.344(6), C(20)–C(21), 1.511(7); C(19)–C(23), 1.482(10); Cl–Pd–S, 94.23(12); S–Pd–N, 82.55(12); N–Pd–C(19), 94.3(2); C(10)–C(11)–N, 123.9(2); C(11)–N–C(12), 117.1(6); C(19)–Pd–Cl, 90.0(2); C(6)–C(20)–C(19), 125.3(4) and C(20)–C(19)–Pd, 128.4(4)].

palladacycle, a five-membered chelate ring formed by the binding of the nitrogen and sulphur to the palladium and the phenyl ring. The seven-membered palladacycle, which is formed by the set of atoms: Pd, N, C(6), C(10), C(11), C(20) and C(19), is not planar. The value of the torsion angle defined by the atoms C(21)–C(20)–C(19) and C(23) [−0.21°] indicates that the two substituents on the alkene are in a *cis*-arrangement. This is the typical distribution of the substituents found for palladium(II) compounds arising from the monoinsertion of alkynes into the σ(Pd–C) bond of palladacycles [11a,b,22].

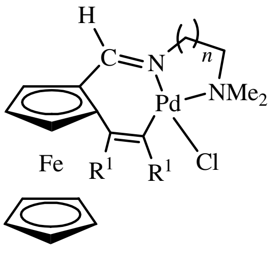
The >C=N– functional group is contained in the seven-membered metallacycle (endocyclic) and forms an angle of 30.1° with the C_5H_3 ring. The >C=N– bond length [1.323(7) Å] is a bit larger than those reported for the free ligand [average value for the two non-equivalent molecules: 1.268(4) Å] or for **1c** [1.296(4) Å] [18].

The five-membered chelate ring has an envelope-like conformation in which the palladium(II) deviates by ca. 0.9147 Å (towards the opposite direction of the iron) from the plane defined by the atoms N, C(12), C(17) and S [23].

The phenyl ring is planar [24] and its mean plane forms angles of 142.0° and 135.0° with the imine moiety and the coordination plane of the molecule, respectively.

The results obtained from the reaction of **1c** with MeO_2C–C≡C–CO_2Me are similar to those reported for **1a** and **1b**, which also underwent the insertion of one molecule of MeO_2C–C≡C–CO_2Me to give [Pd{[(MeO_2C–C=C–CO_2Me)(η^5-C_5H_3)–CH=N–(CH_2)$_n$-(CH_2)–NMe_2]Fe(η^5-C_5H_5)}Cl] [with n = 1 (**2a**) or 2 (**2b**)] (Chart 2), under identical experimental conditions [19].

In order to elucidate the relative importance of the nature of the sulphur atom (in **1c**) or the amine nitrogen (in **1a**) as well as the backbone holding the two heteroatoms [N,N′ (in **1a**) or N,S (in **1c**)] upon the structures of the palladacycles arising from the monoinsertion of the MeO_2C–C≡C–CO_2Me into the σ[Pd–C(sp^2, ferrocene)] bond of **1a** or **1c**, we decided to crystallize [Pd{[(MeO_2C–C=C–CO_2Me)(η^5-C_5H_3)–CH=N–(CH_2)$_2$–NMe_2]Fe(η^5-C_5H_5)}Cl] [19] (**2a**) (Chart 2) and to solve



n = 1 (**2a**) or 2 (**2b**)

Chart 2.

its X-ray crystal structure. The molecular structure of **2a** consists of a 1:1 mixture of: [Pd{[(MeO_2C–C=C–CO_2-Me)(η^5-C_5H_3)–CH=N–$(CH_2)_2$–NMe_2]Fe(η^5-C_5H_5)}Cl] (**2a**) and CH_2Cl_2 molecules.

In the heterodimetallic array (Fig. 2) the palladium(II) is bound to the N(1) and N(2) atoms of the ferrocenyl ligand, a chloride [Cl(1)] and the C(17) carbon of the alkene in a distorted square-planar environment [25]. The N(1)–Pd–N(2) and Cl–Pd–N(2) bond angles [81.19(17)° and 93.35(13)°] are smaller than in **1a** [82.59(18)° and 100.40(14)°, respectively] [16a].

The molecule has a [5,7,5] tricyclic system formed by a five-membered chelate ring, a seven-membered metallacycle and the 1,2-disubstituted pentagonal ring of the ferrocenyl moiety. The five-membered chelate ring has an envelope-like conformation in which the C(13) atom deviates ca. 0.463 Å [towards the "Fe(η^5-C_5H_5)" unit] from the plane defined by the remaining atoms [26].

The seven-membered metallacycle contains the imine group and the >C=C< double bond. The two substituents on the alkene moiety are in a *cis*-arrangement as reflected in the value of the torsion angle C(18)–C(17)–C(16)–C(20) [2.21°].

In contrast with the results obtained for **1a**, **1b** and **1c**, when the reaction was performed under identical experimental conditions using **1d** as starting material, no evidences of any chemical change were detected, even when the refluxing period was increased up to five days. This finding suggests that in **1d** the σ(Pd–C) bond is less reactive than in **1c**.

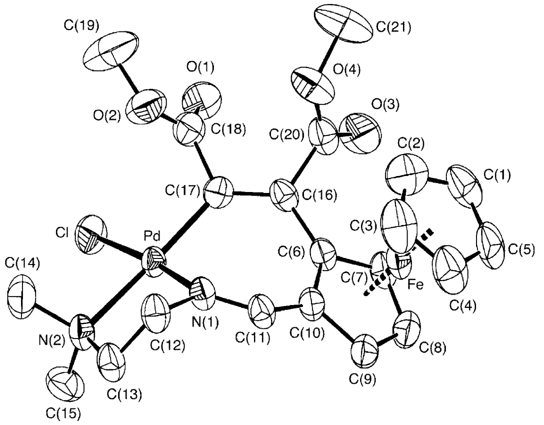


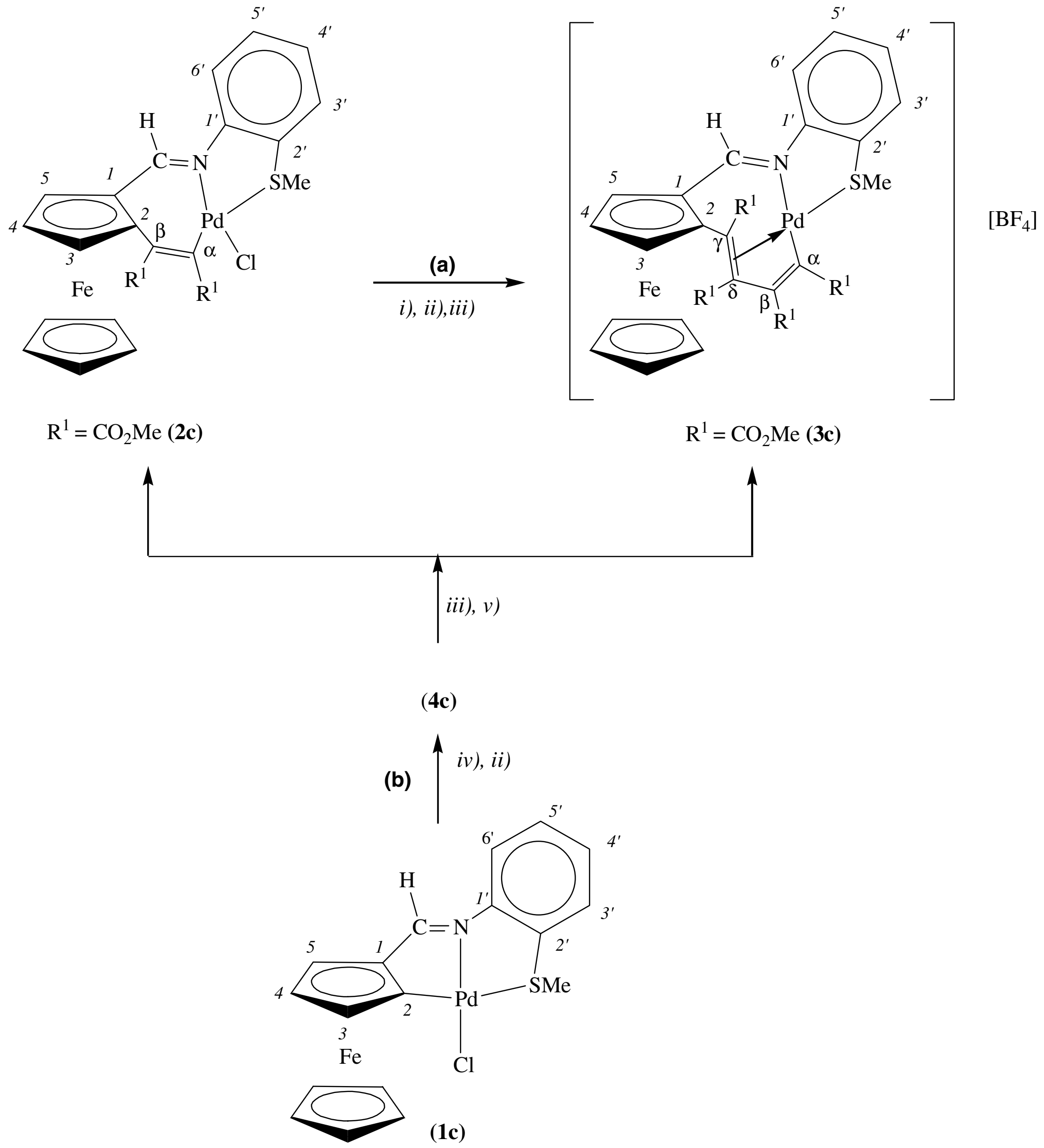
Fig. 2. Molecular structure and atom labeling scheme for compound[Pd{[(MeO_2C–C=C–CO_2Me)(η^5-C_5H_3)–CH=N–$(CH_2)_2$–NMe_2]Fe(η^5-C_5H_5)}Cl] · CH_2Cl_2 (**2a**). The CH_2Cl_2 molecule and the hydrogen atoms have been omitted for clarity. [Selected bond lengths (in Å) and angles (in °): Pd–C(17), 1993(5); Pd–N(1), 2.008(5); Pd–N(2), 2.187(4); Pd–Cl, 2.322(3); N(1)–C(11), 1.277(6); N(1)–C(12), 1.467(6); N(2)–C(14), 1.475(7); N(2)–C(15), 1.482(7); C(6)–C(16),1.471(7); C(16)–C(17), 1.345(7); C(16)–C(20), 1.510(7); C(17)–C(18), 1.484(8); C(17)–Pd–N(1), 94.94(18); N(1)–Pd–N(2), 81.19(17); C(17)–Pd–Cl, 90.69(15); N(2)–Pd–Cl, 93.35(13), C(10)–C(11)–N(1) 126.0(5); C(11)–N(1)–C(12) 118.9(4); C(6)–C(16)–C(17), 107.6(4) and C(16)–C(17)–Pd, 129.7(4)].

In a first attempt to achieve the preparation of the product arising from the bis(insertion) of the alkyne into the σ[Pd–C(sp^2, ferrocene)] of **1c**, we decided to perform two different experiments, which consisted on: (a) the reaction of **1c** and the alkyne in a 1:2 molar ratio or (b) the treatment of **2c** with the stoichiometric amount of and MeO_2C–C≡C–CO_2Me in refluxing CH_2Cl_2 for varying periods (from 2 h to 3 days). However, in the two cases only **2c** was isolated and no evidence of traces of any other palladium(II) complex were detected by NMR. Thus indicating that **2c** is not prone to undergo the insertion of an additional molecule of the alkyne.

When **1c** or **1d** were treated separately with diphenylacetylene or hex-3-yne [in a alkyne: (**1c** or **1d**) molar ratios = 2 or 1] in refluxing CH_2Cl_2 (or $CHCl_3$) for varying reaction periods (from 2 h to 2 days), the corresponding starting materials (**1c** or **1d**) were recovered unchanged and no evidence of any chemical change was detected by NMR. These results reveal that **1a**, **1b** and **1c** are more prone to undergo the insertion of MeO_2C–C≡C–CO_2Me than [Pd{[(MeO_2C–C=C–CO_2Me)(η^5-C_5H_3)–CH=N–$(CH_2)_n$–CH_2–NMe_2]Fe(η^5-C_5H_5)}Cl] [n = 1 (**2a**) or 2 (**2b**)] [19] and **2c** (see Scheme 3).

Previous studies based on the insertion of alkynes into the σ[Pd–C(sp^2, aryl)] bond of cyclopalladated derivatives have shown that the first step of the process involves the coordination of the alkyne to the palladium in a *cis*-arrangement of the metallated carbon atom [11i]. On this basis, the smaller proclivity of **2a**, **2b** and **2c** to undergo the insertion of one molecule of MeO_2C–C≡C–CO_2Me when compared with that of **1a**, **1b** and **1c** could be related to the different lability of the Pd–Cl bond. To check this hypothesis we decided to elucidate whether the removal of the chlorine in **2c**, upon the addition of thallium(I) salts could enhance its reactivity versus MeO_2C–C≡C–CO_2Me [27]. With this aim and as a first approach to the problem, **2c** was treated in acetone with a 50% excess of Tl[BF_4] at ca. 20 °C for 2 h. During this period the precipitation of TlCl was observed. The subsequent removal of the TlCl and the excess of Tl[BF_4] (see Section 3) followed by the treatment of the residue with CH_2Cl_2 and the equimolar amount of the alkyne under reflux for 2 h lead (after concentration to dryness of the resulting deep-purple solution) a solid which was identified as [Pd{[(MeO_2-C–C=C–CO_2Me)$_2$(η^5-C_5H_3)–CH=N–(C_6H_4-2-SMe)]-Fe(η^5-C_5H_5)]} [BF_4] (**3c**) [Scheme 2, step (a)]. Compound **3c** arises from the insertion of one molecule of MeO_2C–C≡C–C–O_2Me into the σ(Pd–C) bond of **2c**, and contains a η^3-butadienyl unit attached to the 1,2-disubstituted pentagonal ring of the ferrocenyl moiety.

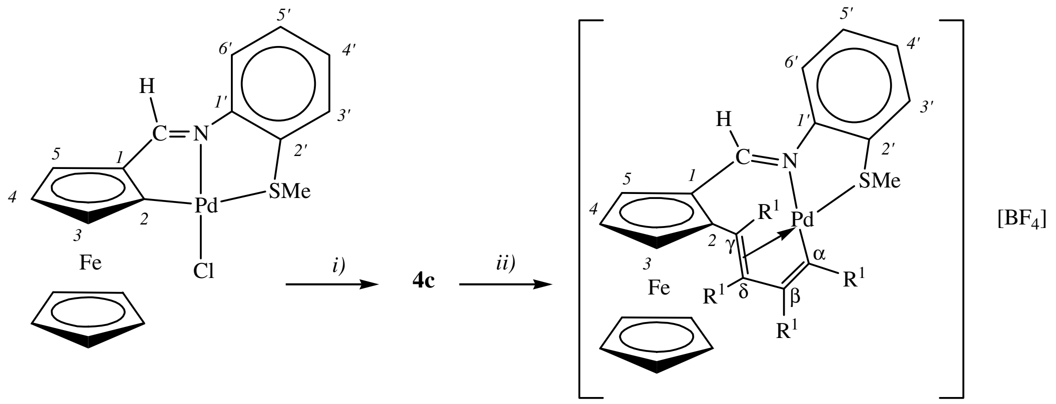
The infrared spectrum of **3c** showed: a sharp and intense band at 1618 cm^{-1}, which is assigned to the stretching of the >C=N– group, the absorptions due to the –CO_2 functional groups and the characteristic bands of the [BF_4]$^-$ anion [28]. The molar conductivity



Scheme 2. (i) $Tl[BF_4]$ in acetone (molar ratio Tl(I)/**2c** = 1.5) at room temperature, (ii) followed by the removal of the TlCl formed and the unreacted $Tl[BF_4]$ using CH_2Cl_2, followed by the subsequent evaporation to dryness. (iii) Addition of the equimolar amount of the alkyne in refluxing CH_2Cl_2 for 2 h. (iv) $Tl[BF_4]$ in acetone (molar ratio Tl(I)/**1c** = 1.5) at room temperature. (v) SiO_2– column chromatography (see text).

of a 10^{-3} M solution of **3c** in acetone [112 $\Omega^{-1}cm^2mol^{-1}$] was consistent with the value expected for a 1:1 electrolyte [29]. The most relevant features observed in the ^{1}H NMR spectrum of **3c** is the presence of four singlets at δ = 3.71, 3.75, 3.94 and 4.01 ppm. In the HSQC spectrum these four signals showed cross-peaks with the resonances at δ = 53.0, 53.6, 54.8 and 55.1 ppm observed in the $^{13}C\{^1H\}$ NMR spectrum. The signals due to the four types of carbon nuclei of the butadienyl unit $\{C^\alpha–C^\delta\}$ appeared at δ = 118.9, 134.9, 135.6 and 149.5 ppm and exhibited low intensity. All these findings are similar to those reported for [Pd$\{[(MeO_2C–C{=}C–CO_2Me)_2(\eta^5\text{-}C_5H_3)–CH{=}N–(CH_2)_n\text{-}(CH_2)–NMe_2]Fe(\eta^5\text{-}C_5H_5)]\}$[BF$_4$] (with n = 1 or 2) [19] (Chart 3) in which the two substituents of the alkene closest to the ferrocenyl unit are in a *trans*-arrangement, while the remaining two CO_2Me groups are in a *cis*-disposition.

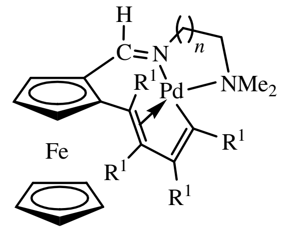
In contrast with the results obtained in the reaction of **2c** with $MeO_2C–C{\equiv}C–CO_2Me$, when **1c** was treated with a 50% excess of $Tl[BF_4]$, followed by the removal of the thallium(I) salts, the subsequent concentration of the filtrate to dryness produced a deep-blue (nearly black) solid (here in after referred to as **4c**). The subsequent treatment of a CH_2Cl_2 solution of this material with $MeO_2C–C{\equiv}C–CO_2Me$ (in a **1c**: alkyne molar ratio 1:2) under reflux for 1 h, lead to a mixture of two compounds [Scheme 2(b)], which could be isolated by SiO_2



(1c)

R^1 = Ph **(5c)** or Et **(6c)**

Scheme 3. (i) $Tl[BF_4]$ in acetone at room temperature for 4 h, followed by filtration and concentration to dryness of the filtrate. (ii) Treatment with the alkyne (diphenylacetylene or hex-3-yne, in a alkyne: **1c** molar ratio = 2) in refluxing CH_2Cl_2 for 2 h, followed by SiO_2 column chromatography (see text).



$R^1 = CO_2Me$
n = 1 **(3a)** or 2 **(3b)**

Chart 3.

column chromatography. Elution with CH_2Cl_2, followed by concentration to dryness of the band collected allowed us to isolate the minor component, whose characterization data were identical to those of **2c**; while the subsequent elution with a mixture CH_2Cl_2:MeOH (100:1) produced the release of an additional deep purple band, which was collected and concentrated to dryness giving **3c**. The molar ratio **3c**:**2c** was 0.5, but when the refluxing period increased up to 2 h the amount of **2c** recovered decreased [molar ratio **3c**:**2c** $\approx$ 9].

These findings agree with the results obtained from the reaction of **2c** with $MeO_2C–C\equiv C–CO_2Me$ in the presence of $Tl[BF_4]$, which also led **3c**, and support the hypothesis that the low lability of the Pd–Cl bond in **2c** hinders the insertion of an additional molecule into the σ[Pd–C(sp^2, alkene)] bond of **2c** to give **3c**.

More interesting were the results obtained when this reaction was repeated using diphenylacetylene or hex-3-yne (molar ratio **1c**: alkyne = 0.5) under identical experimental conditions. In these cases, two different compounds could be isolated by SiO_2-column chromatography. The elution with CH_2Cl_2 allowed to isolate a deep blue solid whose characterisation data was identical to those of the starting material **1c**. The elution with a CH_2Cl_2:MeOH (100:1) mixture produced the release of an additional band. The concentration of the solution gave deep red solids. Their elemental analyses were consistent with those expected for: $[Pd\{[(R^1–C–C=C–R^1)_2(\eta^5-C_5H_3)–CH=N–(C_6H_4–2-SMe)]Fe(\eta^5-C_5H_5)\}[BF_4] \cdot CH_2Cl_2$ [with R^1 = Ph (**5c**), or Et (**6c**)]. Compounds **5c** and **6c** arise from the bis(insertion) of the corresponding alkyne. The FAB$^+$ mass spectra of **5c** and **6c** showed a peak at m/z = 796 and 606, respectively, which are consistent with the values expected for the cationic arrays of these complexes. The infrared spectra of **5c** and **6c** showed the typical bands of the $[BF_4]^-$ anion [28], and a sharp and intense band at 1592 (for **5c**) and 1602 (for **6c**) cm^{-1}, assigned to the imine group. Molar conductivity measurements of 10^{-3} M solutions of **5c** and **6c** [105 and 110 Ω^{-1} cm^2 mol^{-1}, respectively] agreed with the values expected for 1:1 electrolytes [29].

The X-ray crystal structure of **5c** consists of equimolar amounts of the heterobimetallic cations $[Pd\{[(PhC–C=C–Ph)_2(\eta^5-C_5H_3)–CH=N–(C_6H_4–2-SMe)]-Fe(\eta^5-C_5H_5)\}]^+$, $[BF_4]^-$ anions and CH_2Cl_2. In the cation (Fig. 3), the palladium is bound to the nitrogen and the sulphur atoms of the ferroceny ligand, to the terminal carbon of the η^3-butadienyl unit [C(21)] and to the middle point of the segment defined by the atoms C(18) and C(19) (hereinafter referred to as χ) in a slightly distorted square-planar environment [30]. The Pd–N bond distance [2.138(2) Å] is larger than that found for **1c** [2.020(9) Å] and for **2c** [2.030(8) Å]. The Pd–S bond length [2.3011(10) Å] falls in the upper range of the values reported for other palladium(II) thioether derivatives [from 2.24 to 2.31 Å] [31] but it is shorter than in **1c** [2.3653(11) Å]. This may be attributed to the different influence of the ligand in a *trans*-arrangement [32].

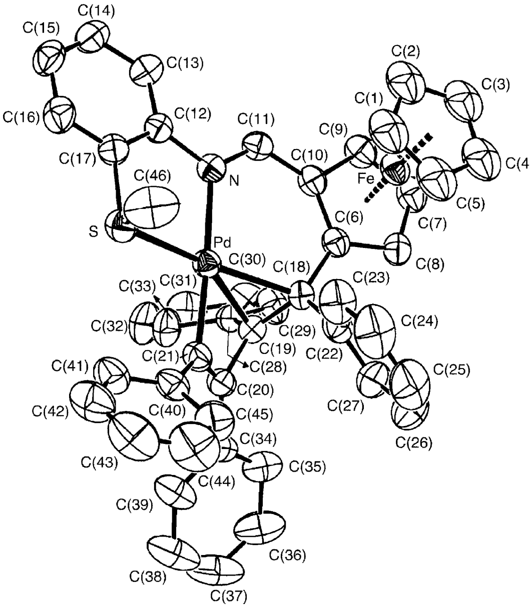


Fig. 3. Molecular structure and atom labelling scheme of the cationic array of [Pd{[(Ph–C=C–Ph)$_2$(η^5-C_5H_3)–CH=N–(C_6H_4-2-SMe)]-Fe(η^5-C_5H_5)}] [BF_4] · CH_2Cl_2 (**5c**). Hydrogen atoms have been omitted for clarity. [Selected bond lengths (in Å) and angles (in °): Pd–N, 2.138(2); Pd–S, 2.3011(10); Pd–C(21), 2.006(3); Pd–C(19), 2.204(3); Pd–C(18), 2.235(3); Pd–χ 2.1049(3); S–C(17), 1.773(3); S–C(46), 1.810(5); C(10)–C(11), 1.426(5); C(11)–N, 1.287(4); C(6)–C(18), 1.489(4); C(18)–C(19), 1.409(4); C(19)–C(20), 1.509(4); C(20)–C(21), 1.330(5); N–Pd–S, 84.17(8); C(21)–Pd–N, 98.2(1), N–Pd–χ, 170.9(1); C(6)–C(10)–C(11), 130.4(3) and C(10)–C(11)–N, 125.7(3)].

The cationic array contains a [5,9,5,6] tetracyclic system formed by the fusion of the substituted pentagonal ring, a nine-membered metallacycle, a five-membered chelate ring and the phenyl ring.

The >C=N– group is contained in the nine-membered metallacycle (*endocyclic*) and the >C=N– bond length [1.287(4) Å] is a bit shorter than that found for **2c** [1.323(7) Å].

The phenyl rings on the double bond [C(18)–C(19)] closest to the ferrocenyl unit are *cis*- to each other while those on the C(20)–C(21) bond are *trans*-. This is the most common distribution of substituents found in related palladacycles arising from bis(insertion) of alkynes into the σ(Pd–C) bond [11,12].The double bond defined by the C(18) and C(19) atoms is placed in the opposite direction of the "Fe(η^5-C_5H_5)" moiety and these two carbon atoms are unsymmetrically bound to the palladium(II), as reflected in the two Pd–C bond lengths [Pd–C(18): 2.235(3) Å and Pd–C(19): 2.204(3) Å].

The five-membered chelate ring formed by the atoms Pd,N(1),C(12),C(17) and S has an envelope-like conformation [33] where the palladium(II) deviates by ca. 0.304 Å {in the opposite direction of the "Fe(η^5-C_5H_5)" moiety} from the mean plane.

In each cation the separation between the C(29)–H(29) bond and the centroid of the substituted pentagonal ring of the ferrocenyl unit (2.790 Å) suggests the existence of a CH···π interaction [34]. Besides that, in the crystal the cationic arrays are associated through C–H···π interactions between the C(44)–H(44) bond of the phenyl ring on the terminal carbon of the η^3-butadienyl unit and the aromatic ring defined by the set of atoms [C(34)–C(39)] of a close cation.

2.2. Attempts to clarify the nature of the intermediate specie 4c

The results presented in the previous paragraphs reveal that reaction of **1c** with MeO_2C–C≡C–CO_2Me in the presence of Tl[BF_4] with the alkyne lead to a mixture of **2c** and **3c**, while when the reaction was performed under identical experimental conditions but using R^1–C≡C–R^1 (R^1 = Ph or Et), the final products were **5c** or **6c** and a nearly invariant amount of the starting material **1c** was also recovered. These findings are similar to those obtained for a parallel study using **1a** or **1b**, for which the formation of the dimeric compounds: [Pd_2{[(η^5-C_5H_3)–CH=N–(CH_2)$_n$–CH_2–NMe_2]Fe(η^5-C_5H_5)}$_2$Cl(acetone)][BF_4]} [with n = 1 (**4a**) or 2 (**4b**) **4b**, 4(a)] has been postulated as intermediate species formed after the treatment of **1a** or **1b** with Tl[BF_4]. In the view of these findings, we were prompted to attempt the characterization of the intermediate specie **4c** [35].

Its infrared spectrum showed the bands due to the [BF_4]$^-$ anion [28] but, its ^{1}H and ^{13}C^{1}H NMR spectra were more complex than that initially expected for the monomeric derivative: [Pd{[(η^5-C_5H_3)-CH=N–(C_6H_4-2- SMe)]Fe(η^5-C_5H_5)}(acetone)][BF_4] which arises from **1c** by abstraction of the Cl$^-$ anion and the coordination of the solvent (acetone). In fact, six different singlets due to the protons and carbon-13 nuclei of the fragments –CH=N–, –SMe and (η^5-C_5H_5) (of relative intensities 1:1:1:1:0.6:0.6) were detected in the ^{1}H NMR spectrum. Elemental analyses of **4c** were consistent with those expected for: {[Pd_2{[(η^5-C_5H_3)-CH=N–(C_6H_4-2-SMe)]-Fe(η^5-C_5H_5)}]$_2$Cl(acetone)][BF_4]}$_n$ and its mass spectrum (MALDI-TOF$^+$) showed a peak at m/z = 917, which could be indicative of the presence of the cation: [Pd{[(η^5-C_5H_3)–CH=N–(C_6H_4-2-SMe)]Fe(η^5-C_5H_5)}$_2$-Cl(acetone)]$^+$. These findings could suggest that the intermediate specie **4c** could have greater nuclearity. On the basis of the characterization data available at this moment [35], we tentatively postulate the formation of the dimeric cations shown in Fig. 4(b). The higher complexity of the ^{1}H and ^{13}C NMR spectra of **4c**, when compared with those of **4a** and **4b** may be attributed to the presence of the SMe group. The transformation of **1c** into **4c** involves the abstraction of the Cl$^-$ anion, the cleavage of the Pd–S bonds of **1c** and the formation of two new Pd–S bonds to achieve the central 10-membered ring. Consequently, and due to the prochiral nature of the tioether group in this process, several isomeric

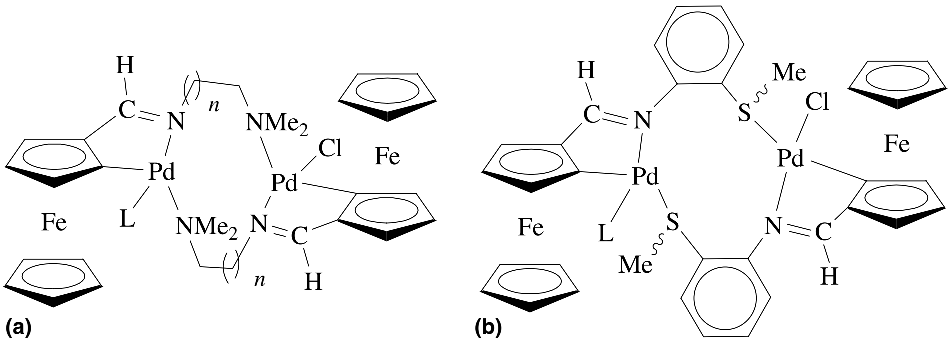


Fig. 4. Schematic views of the cationic arrays of compounds {[{Pd[{(η^5-C_5H_3)–CH=N–$(CH_2)_n$-CH_2–NMe_2}Fe(η^5-C_5H_5)]}$_2$Cl(acetone)][BF_4] {n = 1 (**4a**) or 2 (**4b**)} (a) and [{Pd[{(η^5-C_5H_3)–CH=N–(C_6H_4-2- SMe)}Fe(η^5-C_5H_5)]}$_2$Cl(acetone)][BF_4] (**4c**) (b) (L = acetone).

species of **4c** could be formed. These isomers may differ on: (a) the planar chirality of the two metallated fragments, (b) the chirality of the two –SMe groups and even (c) the relative arrangement of the terminal groups {Cl^- and acetone} in the two halves of the molecule.

2.3. Study of the reactivity of the seven- and nine-membered palladacycles with PPh_3

Some authors have reported that palladacycles arising from the mono- or bis(insertion) of alkynes into the σ(Pd–C) bond are also valuable precursors for the synthesis of novel organic or organometallic derivatives [1,10,12]. One of the most common strategies used to achieve this aim consists of the treatment of the complexes with phosphines (i.e., PPh_3), which promote the depalladation process of the starting material [11k,11l]. In the view of this, we decided to study the reactivity of **2a**, **2c**, **3c**, **5c**–**6c** with PPh_3.

The reaction of **2a** or **2c** with the stoichiometric amount of PPh_3 in CH_2Cl_2 produced the cleavage of the σ(Pd–S) bond (of **2c**) or the σ[Pd–N(amine)] bond (of **2a**) and the incorporation of a phosphine ligand in the coordination sphere of the palladium(II), leading to [Pd{[(MeO_2C–C=C–CO_2Me)(η^5-C_5H_3)–CH=N–$(CH_2)_2$–2-NMe_2]Fe(η^5-C_5H_5)}Cl(PPh_3)] (**7a**) and [Pd{[(MeO_2C–C=C–CO_2Me)(η^5-C_5H_3)–CH=N–$(CH_2)_2$–2-NMe_2]-Fe(η^5-C_5-H_5)}Cl(PPh_3)] (**7c**), respectively (Scheme 4).

When these reactions were performed with **3c**, **5c** or **6c** using the same experimental conditions as for **2c**, no evidence of any chemical change was detected by NMR. In fact, only the resonance due to the free PPh_3 ligand was observed in the $^{31}P\{^1H\}$ NMR spectra. Thus suggesting that **3c**, **5c** and **6c** are less prone to react with PPh_3 than **2c**. Compounds **7** were characterized by the elemental analyses, mass spectrometry, infrared spectra and mono and two dimensional NMR spectroscopy. Elemental analyses (Section 3) agreed with those expected for **7a** and **7c**. Their IR spectra showed three bands in the range 1600–1720 cm^{-1}, one of them was assigned to the stretching of the >C=N– group while the remaining two at lower energies were due to the –COO moiety. The bands of the coordinated PPh_3 ligand were also detected [28,36].

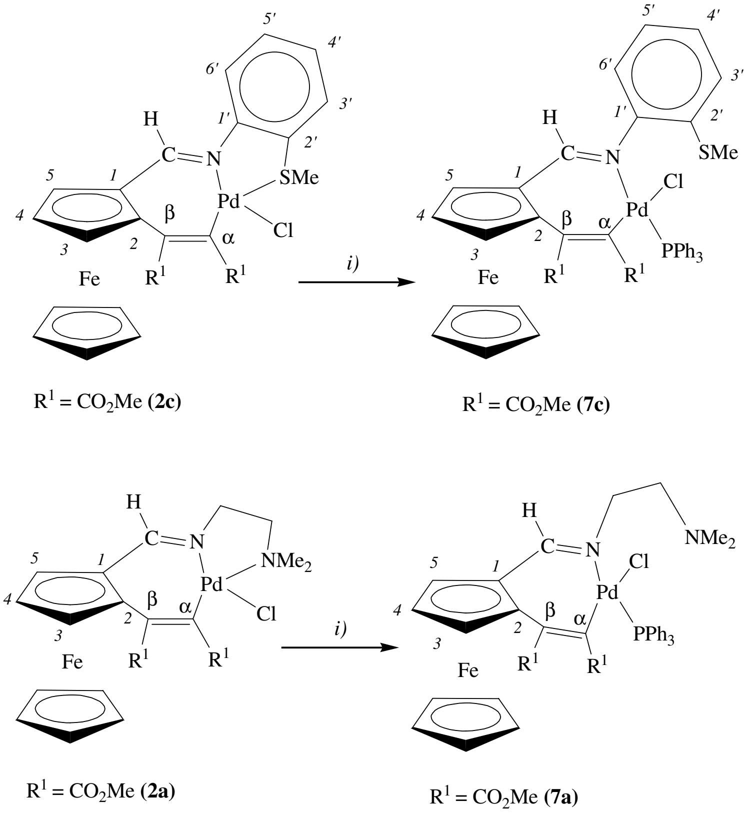
The position of the signal due to the protons of the NMe_2 (in **7a**) or the SMe (in **7c**) groups observed in the ^1H-NMR spectra was very similar to those of the corresponding free ligands. Thus suggesting that the σ(Pd–NMe_2) (in **2a**) or the σ(Pd–S) (in **2c**) bond cleaved during the formation of **7a** and **7c**, respectively. In both cases the signal due to the imine proton appeared as a doublet due to phosphorous coupling. $^{31}P\{^1H\}$ NMR spectra of **7** showed a singlet at $\delta = 27.8$ (for **7a**) and 29.5 (for **7c**) ppm suggested a *cis*-arrangement between the phosphorous atom and the metallated carbon, due to the so-called transphobia effect [37] and the differences observed in the positions of the these signals could be related to the different basicity of the imine nitrogen.

The crystal structure of **7c** consists of equimolar amounts of [Pd{[(MeO_2C–C=C–CO_2Me)(η^5-C_5H_3)–CH=N–(C_6H_4-2-SMe)]Fe(η^5-C_5H_5)}Cl(PPh_3)] and CH_2Cl_2.

In each one of the dimetallic units (Fig. 5), the palladium(II) is bound to the imine nitrogen of the Schiff base, a chlorine, the phosphorous of the PPh_3 ligand and the terminal carbon [C(22)] of the alkene in slightly distorted square-planar environment [38]. The Pd–P bond length [2.2579(8) Å] falls in the range reported for related palladium(II) compounds of the type [Pd(C,N)Cl(PPh_3)], where (C,N) represents a cyclopalladated imine [12g,12j,14b,16,39]. The Pd–N and Pd–Cl(1) bond distances [2.118(2) and 2.3962(8) Å] are slightly larger than those found for **1c** [Pd–N: 2.020(3) and 2.2851(14) Å]. The PPh_3 ligand and the imine nitrogen are in a *trans*-arrangement as reflected in the P–Pd–N bond angle [173.04(8)°].

Each molecule contains a [5,7,5,6] tetracyclic system formed by the 1,2-disubstituted pentagonal ring of the ferrocenyl unit a seven-membered palladacycle which contains the >C=N– functional group, the five-membered chelate ring and the phenyl ring.

The value of the torsion angle: C(20)–C(19)–C(22)–C(23) is 4.85°, indicating that the two identical



Scheme 4. (i) PPh_3 in CH_2Cl_2 at room temperature.

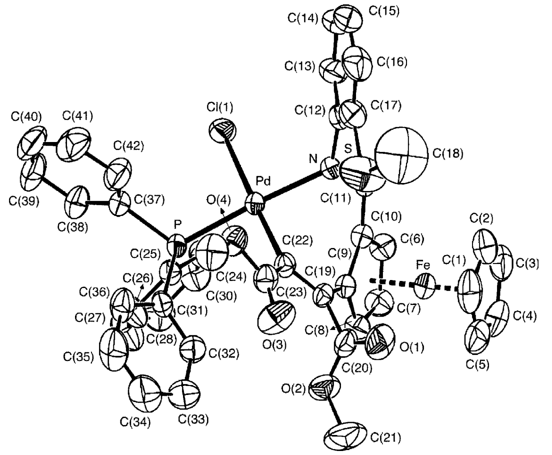


Fig. 5. Molecular structure and atom labelling scheme for $[Pd\{[(MeO_2C{-}C{=}C{-}CO_2Me)(\eta^5{-}C_5H_3){-}CH{=}N{-}(C_6H_4{-}2{-}SMe)]Fe(\eta^5{-}C_5H_5)\}Cl(PPh_3)] \cdot CH_2Cl_2$ (**7c**). The CH_2Cl_2 molecule and the hydrogen atoms have been omitted for clarity. [Selected bond lengths (in Å) and angles (in °): Pd–N, 2.118(2); Pd–P, 2.2579(8); Pd–Cl(1), 2.3962(8); Pd–C(22), 1.999(3); C(10)–C(11) 1.439(4); C(11)–N, 1.280(4); S–C(17), 1.764(5); S–C(18), 1.717(9); C(9)–C(19), 1.471(4); C(19)–C(20), 1.510(4); C(19)–C(22), 1.348(4); C(22)–Pd–N, 88.13(11); P–Pd–C(22), 92.05(9); N–Pd–Cl, 90.18(7); P–Pd–Cl(1), 89.30(3); N–C(12)–C(17), 119.4(3); N–C(11)–C(10), 123.2(3); C(11)–C(10)–C(9), 128.3(3); C(10)–C(9)–C(19), 127.7(3); C(9)–C(19)–C(22), 123.7(3); C(19)–C(22)–Pd, 120.7(2) and C(17)–S–C(18), 104.2(4)]

substituents (the $-CO_2Me$ groups) on the alkene are in a *cis*-disposition.

The aryl ring of the ferrocenyl ligand is planar [40] and its main plane forms angles of 68.7° and 117.2° with the imine moiety and the coordination plane of the palladium(II), respectively.

For the four structures presented here, bond lengths and angles of the "$(\eta^5{-}C_5H_5)Fe(\eta^5{-}C_5H_3)$" fragment are consistent with those found for most ferrocene derivatives [41], and the two pentagonal rings are planar [42] and nearly parallel [tilt angle: 1.1° (for **2a**), 4.2° (for **2c**), 7.9° (for **5c**) and 3.5° (for **7c**)] and they deviate by ca: 3.5° (in **2a**), 10.4° (in **2c**), 29.7° (in **5c**) and 7.15° (in **7c**) from the ideal eclipsed conformation. In all cases the separation between the two metal atoms [5.1553, 5.1189, 4.5033 and 4.9774 Å for **2a**, **2c**, **5c** and **7c**, respectively] are clearly greater than the sum of the van der Waals radii [43] of these atoms, thus suggesting the absence of any direct interaction between the Fe and the Pd.

2.4. Conclusions

The results presented here reveal that despite the different nature and hardness of the terminal X group

[X = N′ (in **1a** and **1b**) or S in **1c**] in a *trans*-arrangement to the metallated carbon of palladacycles with a [C(sp^2, ferrocene),N,X]$^-$ group, the reactivity of **1a**, **1b** and **1c** with R^1–C$\equiv$C–R^1 (R^1 = CO_2Me, Ph or Et) is alike.

In contrast with these findings the results obtained for [Pd{[(η^5-C_5H_3)–CH=N–(C_6H_4-2-SMe)]Fe(η^5-C_5H_5)}-Cl] (**1c**) and [Pd{(2-CH_2–4,6-Me_2–C_6H_2)–CH=N–(C_6H_4–2-SMe)}Cl] (**1d**) [14e], with a mer-[C,N,S]$^-$ ligand, indicated that **1c** is more prone to undergo the insertion of the alkynes than **1d**. The differences observed in the reactivity of **1c** and **1d** may be ascribed to the different lability of the Pd–Cl bond and/or the nature of the metallated carbon [a C(sp^2, ferrocene) in **1c** or a C(sp^3) in **1d**]. The comparison of selected structural data for **1c** and **1d** (Table 1) [14e,18] shows that the Pd–Cl and Pd–C bond lengths in **1d** are larger than in **1c**, and on this basis one would expect a greater lability of these bonds in **1d**. However, the experimental work revealed that under identical experimental conditions **1c** underwent the insertion of MeO_2C–C$\equiv$C–CO_2Me, while **1d** was recovered unchanged. In the view of these facts, other more subtle factors, such as the free space available for the approach of the alkyne to the palladium(II) may also play a crucial role in these reactions. As can be easily seen in Table 1, the S–Pd–Cl and C–Pd–Cl bond angles for **1c** are greater than for **1d**, thus indicating that the environment of the palladium(II) is more constrained in **1d** than in **1c**, and consequently, the approach of the bulky MeO_2C–C$\equiv$C–CO_2Me, is expected to be more difficult in **1d** than in **1c**.

On the other hand, and since it is well known that palladacycles arising from the insertion of alkynes into the σ(Pd–C) bond are valuable precursors for the synthesis of organic or organometallic products [10–12], the new compounds presented in this work appear to be excellent candidates to be studied in this field. Despite the similar reactivity of **1a**, **1b** and **1c** versus the alkynes R^1–C$\equiv$C–R^1 (R^1 = CO_2Me, Et or Ph), depalladation reactions of their derivatives arising from the mono- or bis(insertion) of the three alkynes under study may produce different organic or organometallic compounds. Studies on this area are currently on the way.

Table 1
Selected bond lengths (in Å) and bond angles (in °) around the palladium(II) in [Pd{[(η^5–C_5H_3)–CH=N–(C_6H_4-2-SMe)]Fe(η^5-C_5H_5)}Cl] (**1c**) and [Pd(2-CH_2–4,6-Me_2–C_6H_2)–CH=N–(C_6H_4–2-SMe)]Cl] (**1d**)

	1c[a]	**1d**[b]
Pd–Cl	2.2851(14)	2.313(3)
Pd–C[c]	1.978(5)	2.041(4)
Pd–S	2.3653(11)	2.409(3)
Pd–N	2.020(3)	2.026(4)
C–Pd–Cl	95.52(15)	92.52(14)
Cl–Pd–S	98.83(6)	94.44(10)
S–Pd–N	84.72(8)	80.04(12)
N–Pd–C	81.38(16)	87.47(15)

[a] Data from Ref. [18].
[b] Data from Ref. [14e].
[c] In **1c**, the metallated carbon atoms is a C(sp^2, ferrocene), while in **1d** it is a C(sp^3) atom.

3. Experimental

3.1. Materials and methods

The alkynes: R^1–C$\equiv$C–R^1 (with R^1 = CO_2Me, Ph or Et), PPh_3 and K[PF_6] were obtained from commercial sources and used as received. Compounds **1a**, **1c**, **1d** and **2a** were prepared as described previously [16,18,19]. The solvents were dried and distilled before use [44]. Some of the preparations described below require the use of the *Highly hazardous* materials Tl[BF_4] which should be handled with *Caution*. Tl[BF_4] was synthesized as reported before [45].

Elemental analyses (C, H, N and S) were carried out at the Serveis de Recursos Cientifics i Tècnics (Univ. Rovira i Virgili, Tarragona). Mass spectra MALDI-TOF$^+$ for (**4c**) and FAB$^+$ for the remaining compounds were performed at the Servei d'Espectrometria de Masses (Univ. Barcelona) with a VOYAGER-DE-RP and VG-Quatro instruments, respectively using 2-hydroxybenzoic acid [(DHB), for MALDI-TOF$^+$ and 3-nitrobenzylalcohol [(NBA), for FAB$^+$] as matrix. Molar conductivity measurements of 10^{-3} M solutions of the compounds in acetone were determined at 20 °C with a CRISON microMC2200 conductivity-meter. Infrared spectra were obtained with a Nicolet 400FTIR instrument using KBr pellets. Routine ^{1}H NMR spectra and ^{13}C{^{1}H} spectra were obtained with a Gemini 200 MHz, a Bruker 250-DXR or a Mercury 400 MHz instruments. High resolution ^{1}H NMR spectra and the two dimensional [^{1}H ^{1}H NOESY and COSY and ^{1}H ^{13}C 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. Except were quoted, the solvent used for the NMR studies was $CDCl_3$ (99.8%) and $SiMe_4$ was used as internal reference. ^{31}P{^{1}H} spectra of **7a** and **7c** were obtained with a Bruker 250-DXR instrument in $CDCl_3$ (99.9%) and using trimethylphosphite as reference [δ^{31}P{P(OMe)$_3$} = 140.17 ppm].

3.2. Preparation of the compounds

3.2.1. [Pd{[(MeO_2C–C=C–CO_2Me)(η^5-C_5H_3)-CH=N–(C_6H_4-2SMe)]Fe(η^5-C_5H_5)}Cl] (**2c**)

Complex **1c** (150 mg, 3.14×10^{-4} mol) was dissolved in 20 mL of CH_2Cl_2, then 40 μL (3.12×10^{-4} mol) of MeO_2C–C$\equiv$C–CO_2Me were added. The resulting reaction mixture was refluxed for 2 h and filtered out. The undissolved materials were discarded and the filtrate was concentrated to ca. 10 mL on a rotary evaporator. The dark solution was passed through a short (2 cm × 2.5 cm) SiO_2 column chromatography using a CH_2Cl_2:MeOH (100:0.2 mixture) as eluant. The deep red band eluted was collected and concentrated to dryness on a rotary evaporator. The solid formed was dried in vacuum for 2 days (yield: 161 mg, 82.8%). Characterisation data: Anal. (%) Calc. for $C_{24}H_{22}ClFeNO_4PdS$ (found): C, 46.63 (46.49); H, 3.59(3.41); N, 2.27 (2.23) and S, 5.19 (5.27). MS (FAB^+): *m/z* = 619 $[M - Cl]^+$. IR: 1716 and 1699 (COO); 1602(>C=N–) cm^{-1}. Λ_M (in acetone) = 12 $\Omega^{-1}\,cm^2\,mol^{-1}$. ^1H NMR data (500 MHz) [46]: δ = 8.23 [s, 1H, –CH=N-]; 4.75 [t, 1H, H^3, J = 2.4]; 4.81 [t, 1H, H^4, J = 2.4]; 5.59 [d, 1H, H^5, J = 2.4]; 4.31 [s, 5H, C_5H_5]; 2.85 [s, 3H, SMe], 7.70 [d, 1H, $H^{3'}$, J = 7.5]; 7.42 [t, 1H, $H^{4'}$, J = 7.5]; 7.40 [t, 1H, $H^{5'}$, J = 7.5]; 7.53 [d, 1H, $H^{6'}$, J = 7.5]; 5.12 [s, 2H, CH_2Cl_2]; 3.78 [s, 3H, OMe] and 2.73 [s, 3H, OMe]. $^{13}C\{^1H\}$ NMR data (100.58 MHz) [46]: δ = 165.2 [>C=N–]; 78.4 [C^1]; 73.1 [C^2]; 77.1 [C^3]; 74.6 [C^4]; 77.3 [C^5]; 71.0 [C_5H_5]; 22.9 [–SMe]; 155.2 [$C^{1'}$]; 130.5 [$C^{2'}$]; 120.4 [$C^{3'}$]; 130.6 [$C^{4'}$]; 129.5 [$C^{5'}$]; 131.1 [$C^{6'}$]; 51.8 [OMe]; 51.7 [OMe]; 171.8 and 172.7 [COO] and 130.2 and 146.2 [C^α and C^β, respectively].

3.2.2. *[Pd{[(MeO₂–C=C–CO₂Me)₂(η⁵-C₅H₃)–CH=N–(C₆H₄–2-SMe)]Fe(η⁵-C₅H₅)}] [BF₄] (3c)*

This complex can be prepared using two different procedures which differ in the nature of the starting material **1c** or **2c**.

Method a. Compound **1c** (150 mg, 3.14×10^{-4} mol) was dissolved in 20 mL of acetone, then 137 mg (4.7×10^{-4} mol) of $Tl[BF_4]$ were added. The reaction mixture was stirred at ca. 20 °C for 4 h and then filtered out to remove the TlCl formed. The filtrate was concentrated to dryness on a rotary evaporator and the deep blue residue was dissolved in 20 mL of CH_2Cl_2. Then 80 µL (7.28×10^{-4} mol) of $MeO_2C–C\equiv C–CO_2Me$ were added dropwise at room temperature. Once the addition had finished, the reaction mixture was refluxed for 2 h. After this period it was filtered out and concentrated to dryness on a rotary evaporator. The gummy residue was dissolved in 10 mL of CH_2Cl_2 and passed through a short SiO_2 column chromatography (2.5 cm × 3.0 cm). The elution with CH_2Cl_2 produced a deep red band which was concentrated to dryness giving **2c** (11 mg). Once this band was collected a CH_2Cl_2/MeOH (100: 1) mixture was used, and the band released lead, after work up, **3c**, which was dried in vacuum for 2 days (yield: 137 mg).

Method b. A 100 mg amount of **2c** (1.62×10^{-4} mol) was dissolved in 20 mL of acetone, then $Tl[BF_4]$ (71 mg, 12.4×10^{-4} mol) was added. The reaction mixture was stirred at ca. 20 °C for 4 h and then filtered out to remove the TlCl formed. The filtrate was concentrated to dryness on a rotary evaporator. The residue was treated with ca. 20 mL of CH_2Cl_2 and stirred at room temperature for 15 min and then filtered out. The undissolved materials were discarded. Then 18 µL (1.64×10^{-4} mol) of $MeO_2C–C\equiv C–CO_2Me$ were added dropwise to the filtrate and the reaction mixture was then refluxed for 2 h. Then, the solution was filtered out and the filtrate was concentrated to dryness on a rotary evaporator. The isolated solid was purified by SiO_2-column chromatography using a CH_2Cl_2/MeOH (100:1) mixture as eluant (yield: 47 mg, 71.2%).

Characterisation data for **3c**: Anal. (%) Calc. for $C_{30}H_{28}BF_4FeNO_8PdS$ (found): C, 44.39 (44.60); H, 3.48 (3.62); N, 1.73 (1.85) and S, 3.95 (4.04). MS (FAB^+): *m/z* = 724 $\{M - [BF_4]^-\}^+$. IR: 1732 [br. (COO)] and 1618 (>C=N–) cm^{-1} Λ_M (in acetone) = 112 $\Omega^{-1}\,cm^2\,mol^{-1}$. ^1H NMR data (500 MHz) [46]: δ = 8.72[s, 1H, –CH=N–]; 4.60 [s, 1H, H^3]; 4.93 [s, 1H, H^4], 5.60 [s, 1H, H^5]; 4.36 [s, 5H, C_5H_5]; 7.49[dd, 1H, $H^{3'}$, J = 7.5, J = 1.0]; 7.23 [td,1H, $H^{4'}$, J = 7.5, J = 1.0]; 7.23 [td, 1H, $H^{4'}$, J = 7.5, J = 1.0]; 7.40 [td, 1H, $H^{5'}$, J = 7.5, J = 1.0]; 7.64 [dd, 1H, $H^{6'}$, J = 7.5, J = 1.0]; 3.71, 3.75, 3.94 and 4.01 [4s, 12H, 4-OMe].$^{13}C\{^1H\}$ NMR data (100.58 MHz) [46]: δ = 167.4 [–CH=N–]; 89.2 [C^1]; 87.5 [C^2]; 75.0 [C^3]; 74.8 [C^4]; 76.2 [C^5]; 72.1 [C_5H_5]; 152.8 [$C^{1'}$]; 122.5 [$C^{2'}$]; 121.4 [$C^{3'}$]; 128.3 [$C^{4'}$]; 131.4 [$C^{5'}$]; 135.6 [$C^{6'}$]; 53.0, 53.6, 54.9 and 55.1[4 OMe];158.8, 163.9, 166.6 and 168.2 [4-COO] and 118.9, 134.9, 135.6 and 149.5 [C^α, C^β, C^δ and C^γ].

3.2.3. *[Pd{[(R¹–C=C–R¹)₂(η⁵-C₅H₃)–CH=N–(C₆H₄–2-SMe)]Fe(η⁵-C₅H₅)}][BF₄] · CH₂Cl₂ [with R¹ = Ph (5c), Et (6c)]*

To a solution containing 150 mg (3.14×10^{-4} mol) of **1c** and 20 mL of acetone an excess of$Tl[BF_4]$ (137 mg, 4.7×10^{-4} mol) was added. The reaction mixture was stirred at ca. 20 °C for 4 h. After the removal of the TlCl formed by filtration, the filtrate was concentrated to dryness on a rotary evaporator. The residue was treated with 20 mL of CH_2Cl_2 and filtered out to remove the excess of $Tl[BF_4]$ and then 6.8×10^{-4} mol of the corresponding alkyne: $R^1–C\equiv C–R^1$ (R^1 = Et or Ph) were added slowly to the deep-blue (nearly black) filtrate. Once the addition had finished, the reaction mixture was refluxed for 2 h. After this period the resulting deep purple solution was filtered out and passed through a short SiO_2-column chromatography (2.5 cm × 3.0 cm). Elution with CH_2Cl_2 produced the release of a deep-blue band which lead after concentration to dryness to small amounts of **1c** [49mg (for R^1 = Ph) and 52 mg (for R^1 = Et)]. The desired complexes **5c** or **6c** were isolated after the subsequent elution with a CH_2Cl_2:MeOH (100:1) mixture and concentration to dryness of the collected red bands. Yields: 98 mg (for **5c**) and 79mg (for **6c**). Characterisation data for **5c**: Anal. (%) Calc. for $C_{45}H_{36}BF_4FeNPdS \cdot CH_2Cl_2$ (found):

C, 58.27(58.32); H, 3.95(4.11); N, 1.45(1.51) and S, 3.31(3.51). MS (FAB$^+$): $m/z = 796$ {M – {$[BF_4]^-$ and CH_2Cl_2}}$^+$. IR: 1592 (>C=N–) cm^{-1}. Λ_M (in acetone) = 105 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR data (500 MHz) [46]: $\delta = 9.25$ [s, 1H, –CH=N–]; 5.18 [t, 1H, H^3, $J = 2.5$]; 5.06 [t, 1H, H^4, $J = 2.5$]; 5.30 [d, 1H, H^5, $J = 2.5$]; 3.82 [s, 5H, C_5H_5]; 2.25 [s, 3H, SMe]; 6.96 [d, 1H, H$^{3\prime}$]; 5.12 [s, 2H, CH_2Cl_2]; 7.17–8.20 [br. m., 23H, H$^{4\prime}$, H$^{5\prime}$, H$^{6\prime}$ and 20 protons of the phenyl ring of the R^1 group]. ^{13}C{^{1}H} NMR data (100.58 MHz) [46,47]: $\delta = 164.0$ [>C=N–]; 88.1 [C^1]; 71.6 [C^2]; 77.5 [C^3]; 74.8 [C^4]; 75.7 [C^5]; 73.0 [C_5H_5]; 26.2 [-SMe],and 146.1, 136.2, 132.4 and 120.1 [C$^\alpha$, C$^\beta$, C$^\delta$, C$^\gamma$, respectively]. For **6c**: Anal. (%) Calc. for $C_{30}H_{36}BF_4FeNPdS \cdot CH_2Cl_2$ (found): C, 47.94 (48.05); H, 4.93 (5.03); N, 1.80 (2.02) and S, 4.13 (4.38). MS (FAB$^+$): $m/z = 606$ [M – $[BF_4]^-$ and CH_2Cl_2]$^+$. IR: 1602 (>C=N–) cm^{-1}. Λ_M (in acetone) = 110Ω^{-1}cm^{2}mol^{-1}}.]$^+$. ^{1}H NMR data (500 MHz) [46]: $\delta = 9.28$ [s, 1H, –CH=N–]; 4.63 [t, 1H, H^3, $J = 2.4$]; 4.89 [t, 1H, H^4, $J = 2.4$]; 5.40 [d, 1H, H^5, $J = 2.4$]; 4.43 [s, 5H, C_5H_5], 2.76 [s, 3H, SMe]; 7.61 [d, 1H, H$^{3\prime}$, $J = 7.5$]; 7.64 [t, 1H, H$^{4\prime}$, $J = 7.5$]; 7.32 [t, 1H, H$^{5\prime}$, $J = 7.5$]; 8.32 [d, 1H, H$^{6\prime}$, $J = 7.5$]; 2.06, 2.46, 2.30 and 2.06 [4m, 8H, –CH$_2$–(Et)];0.88, 0.94,1.18, 1.42 [4t, 12H, CH$_3$ (Et)] and 5.12 [s, 2H, CH_2Cl_2]. ^{13}C{^{1}H} NMR data (100.58 MHz) [46]: $\delta = 166.2$. [>C=N–]; 87.9 [C^1]; 78.4 [C^2]; 74.7 [C^3]; 74.5 [C^4]; 75.9 [C^5]; 71.9 [C_5H_5]; 22.4 [–SMe]; 150.4 [C$^{1\prime}$]; 132.4 [C$^{2\prime}$]; 120.1 [C$^{3\prime}$]; 128.1 [C$^{4\prime}$]; 131.2 [C$^{5\prime}$], 135.3 [C$^{6\prime}$]; 25.8, 26.0, 28.6, 34.5 [–CH$_2$ (Et)]; 12.6, 15.2, 15.3 and 16.9 [CH$_3$ (Et)] and 99.1, 117.5, 143.0 and 143.2 [C$^\alpha$, C$^\beta$, C$^\delta$, C$^\gamma$, respectively].

3.2.4. *[Pd{[(MeO$_2$C–C=C–CO$_2$Me)(η^5-C$_5$H$_3$)–CH=N–(C$_6$H$_4$-2-SMe)]Fe(η^5-C$_5$H$_5$)}Cl(PPh$_3$)] · CH$_2$Cl$_2$ (7c)*

To a solution formed by 40 mg (6.5×10^{-5} mol) of **2c** and 10 mL of CH_2Cl_2, PPh_3 (17 mg, 6.5×10^{-5} mol) was added. The reaction mixture was stirred at ca. 20 °C for 30 min. After this period, the solution was filtered out and slow evaporation of the solvent gave orange crystals suitable for X-ray diffraction, which were collected and air-dried. Yield: 54 mg, 86%. Characterisation data. Anal. (%) Calc. for: $C_{42}H_{37}ClFeNO_4PPdS \cdot CH_2Cl_2$ (found): C, 53.50 (53.62); H, 4.07 (4.12); N, 1.45 (1.40) and S, 3.32 (3.40). MS (FAB$^+$): $m/z = 844$ [M – Cl]$^+$. IR: 1717 and 1698 (COO); 1617 (>C=N–) cm^{-1}. Λ_M (in acetone) = 15 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR data (500 MHz) [46]: $\delta = 7.90$ [d, 1H, –CH=N–, $^4J_{(P-H)} = 8.2$]; 3.90 [t, 1H, H^3, $J = 2.6$ Hz]; 4.65 [t, 1H, H^4, $J = 2.6$Hz]; 4.90 [d, 1H, H^5, $J = 2.6$ Hz]; 4.29 [s, 5H, C_5H_5]; 2.39 [s, 3H, –SMe]; 6.62 [dd, 1H, H$^{3\prime}$, $J = 7.5$, $J = 1.0$]; 5.12 [s, 2H, CH_2Cl_2]; 7.32–7.85 [br.m, 18H, H$^{4\prime}$, H^5, H$^{6\prime}$ and protons of the PPh$_3$ ligand]; 3.72 [s, 3H, OMe] and 3.17 [s, 3H, OMe]. ^{31}P{^{1}H} NMR data: $\delta = 29.5$ ppm.

3.2.5. *Pd{[(MeO$_2$C–C=C–CO$_2$Me)(η^5-C$_5$H$_3$)–CH=N–(CH$_2$)$_2$–NMe$_2$]Fe(η^5-C$_5$H$_5$)}Cl(PPh$_3$)] (7**a**)*

This complex was prepared according to the procedure described above for **7c** but using the stoichiometric amount of [Pd{[(MeO$_2$C–C=C–CO$_2$Me)(η^5-C$_5$H$_3$)–CH=N–(CH$_2$)$_2$–NMe$_2$]Fe(η^5-C$_5$H$_5$)}Cl] (**2a**) as starting material. Yield: 41 mg, 81%. Characterisation data. Anal. (%) Calc. for: $C_{39}H_{40}N_2O_4FePdPCl$ (found): C, 56.48 (56.60); H, 4.86 (5.05) and N, 3.80 (3.68). MS (FAB$^+$): $m/z = 793$ [M – Cl]$^+$. IR: 1716 and 1699 (COO); 1602 (>C=N–) cm^{-1}. Λ_M (in acetone) = 9 Ω^{-1}cm^{2}mol^{-1}. ^{1}H NMR data (500 MHz) [46]: $\delta = 8.20$ [d, 1H, –CH=N–, $^4J_{(P-H)} = 10.6$]; 4.52 [t, 1H, H^3, $J = 2.6$]; 4.79 [t, 1H, H^4, $J = 2.6$]; 4.89 [d, 1H, H^5, $J = 2.6$]; 4.19 [s, 5H, C_5H_5], 2.28 [s, 6H, NMe$_2$]; 4.58 and 3.50 [br.m, 2H, =N–CH$_2$–], 3.05 and 2.58 [br.m, 2H, –CH$_2$–N–]; 3.64 [s, 3H, OMe] and 3.22 [s, 3H, OMe]. ^{31}P{^{1}H} NMR data: $\delta = 27.8$ ppm.

3.3. *Crystallography*

A prismatic crystal of **2a**, **2c**, **5c** or **7c** (sizes in Table 2) was selected an mounted on a ENRAF-CAD diffractometer (for **2a**) or on a MAR345 diffractometer (for **2c**, **5c** and **7c**). For **2a**, unit cell parameters were determined from automatic centering of 25 reflections in the range $12° \leqslant \Theta \leqslant 21°$ and refined by full matrix-least.squares method. For **2c**, **5c** and **7c**, unit-cell parameters were determined from 27,781 reflections (for **2c**), 27,215 (for **5c**) and 34,465 (for **7c**) (in the range $3° < \Theta < 31°$) and refined by least-squares method. Intensities were collected with graphite monochromatized Mo K$_\alpha$ radiation. The number of reflections measured was: 16,228 (in the range $2.35° \leqslant \Theta \leqslant 30.04°$) for **2a**, 75,647 (in the range $2.45° \leqslant \Theta \leqslant 31.60°$) for **2c**, 27,215 (in the range $2.89° \leqslant \Theta \leqslant 31.51°$) for **5c** and 46,268 (in the range $1.67° \leqslant \Theta \leqslant 31.63°$) for **7c**; of which 7379 (for **2a**), 2295 (for **2c**), 9506 (for **5c**) and 13,070 (for **7c**) were non-equivalent by symmetry [R_{int} (on I) = 0.041 (for **2a**), 0.053 (for **2c**), 0.019 (for **5c**) and 0.038 (for **7a**)]. The number of reflections assumed as observed applying the condition $I > 2\sigma(I)$ was 3827 (for **2a**), 2107 (for **2c**), 9506 (for **5c**), 11979 (for **7c**). Lorentz-polarization corrections were made but absorption corrections were not.

The structure was solved by direct methods using SHELXS computer program [48] and refined by full-matrix least-squares method with the SHELX97 computer program [49] using 2295 (for **2a**), 7379 (for **2c**), 10,092 (for **5c**) or 13070 (for **7c**) reflections (very negative intensities were not assumed). The function minimized was $\sum w||F_o|^2 - |F_c|^2|^2$, where $w = [\sigma^2(I) + 0.0684P^2]^{-1}$ (for **2a**), $w = [\sigma^2(I) + 0.0619P^2 + 0.5401P]^{-1}$ (for **2c**), $w = [\sigma^2(I) + 0.0460P)^2 + 7.2802P]^{-1}$ (for **5c**) and $w = [\sigma^2(I) + 0.0643P)^2 + 4.8020P]^{-1}$ (for **7c**) and $P = (|F_o|^2 + 2|F_c|^2)/3$; f, f' and f'' were taken from the literature [50].

Table 2
Crystallographic data and details of the refinement of the cystal structures of $[Pd\{[(MeO_2C{-}C{=}C{-}CO_2Me)(\eta^5{-}C_5H_3){-}CH{=}N{-}(C_6H_4{-}2{-}SMe)]Fe(\eta^5{-}C_5H_5)\}Cl]$ (**2c**), $[Pd\{[(MeO_2C{-}C{=}C{-}CO_2Me)(\eta^5{-}C_5H_3){-}CH{=}N{-}(CH_2)_2{-}NMe_2]Fe(\eta^5{-}C_5H_5)\}Cl]CH_2Cl_2$ (**2a**), $[Pd\{[(Ph{-}C{-}C{=}C{-}Ph)_2(\eta^5{-}C_5H_3){-}CH{=}N{-}(C_6H_4{-}2{-}SMe)]Fe(\eta^5{-}C_5H_5)\}][BF_4] \cdot CH_2Cl_2$ (**5c**), $[Pd\{[(MeO_2C{-}C{=}C{-}CO_2Me)(\eta^5{-}C_5H_3){-}CH{=}N{-}(C_6H_4{-}2{-}SMe)]Fe(\eta^5{-}C_5H_5)\}Cl\ (PPh_3)] \cdot CH_2Cl_2$ (**7c**)

	2c	**2a**	**5c**	**7c**
Empirical formula	$C_{24}H_{22}ClFeNO_4PdS$	$C_{21}H_{25}ClFeN_2O_4Pd \cdot CH_2Cl_2$	$C_{46}H_{36}BF_4FeNPdS \cdot CH_2Cl_2$	$C_{42}H_{37}ClFeNO_4PPdS \cdot CH_2Cl_2$
Formula weight	618.19	652.06	968.81	965.38
T (K)	293(2)	293(2)	293(2)	293(2)
λ (Å)	0.71073	0.71069	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Crystal dimensions (mm × mm × mm)	0.1 × 0.1 × 0.2	0.1 × 0.1 × 0.2	0.1 × 0.1 × 0.2	0.1 × 0.1 0.2
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/n$
a (Å)	20.31(6)	17.405(3)	9.2480(10)	19.8620(10)
b (Å)	9.10(2)	8.657(11)	11.5140(10)	10.5330(10)
c (Å)	12.82(3)	22.830(3)	39.7400(10)	20.7080(10)
α (°)	90.0	90.0	90.0	90.0
β (°)	92.90(8)	130.743(10)	92.040(10)	106.270(10)
γ (°)	90.0	90.0	90.0	90.0
Z	4	4	4	4
V (Å^3)	2366(10)	2006(3)	4228.9(6)	4158.7(5)
D (mg × m^{-3})	1.735	1.662	1.522	1.542
μ (mm^{-1})	1.606	1.584	0.996	1.106
F(000)	1240	1312	1960	1960
Θ Range for data collection (°)	2.45 to 31.60	2.35 to 30.04	2.89 to 31.51	1.67 to 31.63
Number of reflections collected	75647	16228	16219	46268
Number of unique reflections [R(int)]	2295 [0.0534]	7379 [0.0417]	10,092 [0.0196]	13,070 [0.0382]
Number of data	2295	7379	10,092	13,070
Number of parameters	292	306	597	577
Goodness-of-fit on F^2	1.065	0.978	1.092	1.241
Final R indices [$I > \sigma(I)$]	$R_1 = 0.0322$ $wR_2 = 0.0878$	$R_1 = 0.0603$ $wR_2 = 0.1209$	$R_1 = 0.0537$ $wR_2 = 0.1280$	$R_1 = 0.0592$ $wR_2 = 0.1498$
R indices (all data)	$R_1 = 0.0363$ $wR_2 = 0.0911$	$R_1 = 0.1490$ $wR_2 = 0.1506$	$R_1 = 0.0575$ $wR_2 = 0.1309$	$R_1 = 0.0664$ $wR_2 = 0.1540$
Largest difference peak and hole (e Å^{-3})	0.226 and −0.345	0.566 and −0.537	0.859 and −0.744	0.769 and −0.744

Standard deviation parameters are given in parenthesis.

The number of hydrogen atoms located from a difference synthesis was 2 (for **2a**), 13 (for **5c**) and 18 (for **7c**) and they were refined with an overall isotropic temperature factor. The number of hydrogen atoms computed and refined using an isotropic temperature factor equal to 1.2 times the equivalent temperature factor of the atom linked to it was: 25 (for **2a**), all (for **2c**), 23 (for **5c**) and 19 (for **7c**). The final R(on F) factor were 0.060 (**2a**), 0.032 (**2c**), 0.057 (**5c**) and 0.059 (**7c**), wR (on F^2) = 0.120 (**2a**), 0.088 (**2c**), 0.130 (**5c**) and 0.250 (**7c**) and the goodness-of-fit was: 0.978, 1.065, 1.091 and 1.241 for **2a**, **2c**, **5c** and **7c**, respectively.

4. Supplementary materials

Crystallographic data for the structural analyses of **2a** and **2c**, **5c** and **7c** have been depoisted at the Cambridge Crystallographic Data Centre, CCDC, Nos.: 236374, 236375, 236376 and 236377. 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.ccdc.cam.ac.uk).

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