



Cyclopalladation of *N*-phenyl-4-ferrocenylmethylpyrazoles: Crystal structure of $[\text{Pd}\{\kappa^2\text{-C}_3\text{N-C}_6\text{H}_4\text{-1-}[(3,5\text{-Me}_2\text{-C}_3\text{N}_2)\text{-CH}_2\text{-}(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)]\}\text{Cl}(\text{PPh}_3)] \cdot \text{CH}_2\text{Cl}_2$

Asensio González^a, Concepción López^{b,*}, Xavier Solans^c, Mercè Font-Bardía^c, Elies Molins^d

^aLaboratori Química Orgànica, Facultat de Farmàcia, Universitat de Barcelona, Pl. Pius XII s/n, 08028 Barcelona, Spain

^bDepartament de Química Inorgànica, Facultat de Química, Universitat de Barcelona, Martí i Franquès 1-11, E-08028 Barcelona, Spain

^cDepartament de Cristal·lografia Mineralogia i Dipòsits Minerals, Facultat de Geologia, Universitat de Barcelona, Martí i Franquès s/n, E-08028 Barcelona, Spain

^dInstitut de Ciència de Materials de Barcelona (ICMAB-CSIC). Campus de la Universitat Autònoma de Barcelona, 08193 Bellaterra, Spain

ARTICLE INFO

Article history:

Received 15 January 2008

Received in revised form 22 February 2008

Accepted 22 February 2008

Available online 10 March 2008

Keywords:

Cyclopalladation
Ferrocene derivatives
Alkyne insertions
Palladacycles

ABSTRACT

The synthesis and characterization of pyrazole derivatives of general formula $[\text{C}_6\text{H}_4\text{-4-R-1-}[(3,5\text{-Me}_2\text{-C}_3\text{N}_2)\text{-CH}_2\text{-}(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)]]$ [R = OMe (**1a**) or H (**1b**)] with a ferrocenylmethyl substituent are described. The study of the reactivity of compounds **1** with palladium(II) acetate has allowed the isolation of complexes $(\mu\text{-AcO})_2[\text{Pd}\{\kappa^2\text{-C}_3\text{N-C}_6\text{H}_3\text{-4-R-1-}[(3,5\text{-Me}_2\text{-C}_3\text{N}_2)\text{-CH}_2\text{-}(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)]]_2$ (**2**) [R = OMe (**2a**) or H (**2b**)] that contain a bidentate $[\text{C}(\text{sp}^2, \text{phenyl}), \text{N}]^-$ ligand and a central “Pd($\mu\text{-AcO}$)₂Pd” unit. Furthermore, treatment of **2** with LiCl produced complexes $(\mu\text{-Cl})_2[\text{Pd}\{\kappa^2\text{-C}_3\text{N-C}_6\text{H}_3\text{-4-R-1-}[(3,5\text{-Me}_2\text{-C}_3\text{N}_2)\text{-CH}_2\text{-}(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)]]_2$ (**3**) [R = OMe (**3a**) or H (**3b**)] that arise from the replacement of the acetato ligands by the Cl[−]. Compounds **2** and **3** also react with PPh₃ giving the monomeric complexes $[\text{Pd}\{\kappa^2\text{-C}_3\text{N-C}_6\text{H}_3\text{-4-R-1-}[(3,5\text{-Me}_2\text{-C}_3\text{N}_2)\text{-CH}_2\text{-}(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)]]\text{X}(\text{PPh}_3)]$ {X[−] = AcO[−] and R = OMe (**5a**) or H (**5b**) or X[−] = Cl[−] and R = OMe (**6a**) or H (**6b**)}, where the phosphine is in a *cis*-arrangement to the metallated carbon atom. Treatment of **3** with thallium(I) acetylacetonate produced $[\text{Pd}\{\kappa^2\text{-C}_3\text{N-C}_6\text{H}_3\text{-4-R-1-}[(3,5\text{-Me}_2\text{-C}_3\text{N}_2)\text{-CH}_2\text{-}(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)]](\text{acac})$ (**7**) [R = OMe (**7a**) or H (**7b**)]. Electrochemical studies of the free ligands and the cyclopalladated complexes are also reported. The dimeric complexes **3** also react with MeO₂C–C≡C–CO₂Me (in a 1:4 molar ratio) giving $[\text{Pd}\{(\text{MeO}_2\text{C-C}\equiv\text{C-CO}_2\text{Me})_2\text{C}_6\text{H}_3\text{-4-R-1-}[(3,5\text{-Me}_2\text{-C}_3\text{N}_2)\text{-CH}_2\text{-}(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)]\}\text{Cl}]$ (**8**) [R = OMe (**8a**) or H (**8b**)], which arise from the bis(insertion) of the alkyne into the $\sigma\{\text{Pd-C}(\text{sp}^2, \text{phenyl})\}$ bond of **3**.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

An important area of organometallic chemistry is that focused on cyclopalladated complexes. Interest in such compounds has increased exponentially due to their physical and/or chemical properties or their applications in different areas [1–6]. Metallo-mesogens [1c] and antitumor drugs containing palladacycles [3] have been reported. The use of chiral cyclopalladated complexes for the determination of enantiomeric excesses of chiral reagents has also been described [1d]. More recently, examples of their utility in homogeneous catalysis or as building blocks in macromolecular chemistry have also been published [4,6g,6h]. In addition, the high reactivity of the Pd–C bond in this sort of compounds makes them valuable precursors in organic synthesis [1e,1f,5,6b] including the total synthesis of natural products [1e,1f,1g,5d,6b].

On the other hand, ferrocene derivatives containing heterocyclic systems have attracted great interest in recent years [5d,6d,6g,6h,6i–8] because of their physical or chemical physical properties as well as for their applications in a wide variety of areas including homogeneous catalysis [5d,6h,6i] and *Bio-Medicine* [8]. In this sort of compounds, the presence of a heterocycle with one or more atoms with good donor abilities is especially relevant in view to their use as ligands for transition metals to give heteropolymetallic complexes [6g,9,10] in which the existence of two or more metal ions in close vicinity may induce a co-operative effect. Among all the examples reported so far, those containing oxazoline or oxazine rings (Fig. 1A and B) and palladium(II) are specially relevant for different reasons [6g,6h,9]. This type of ligands exhibit an interesting, and sometimes unexpected, coordination modes toward palladium(II). For instance, the reaction of the 4-ferrocenyl-1,3-oxazolines shown in Fig. 1A with palladium(II) acetate gave the unexpected transannular metallation of the non-substituted ring of the ferrocenyl unit giving the pentametallic complex depicted in Fig. 1C [6h].

* Corresponding author.

E-mail address: conchi.lopez@qi.ub.es (C. López).

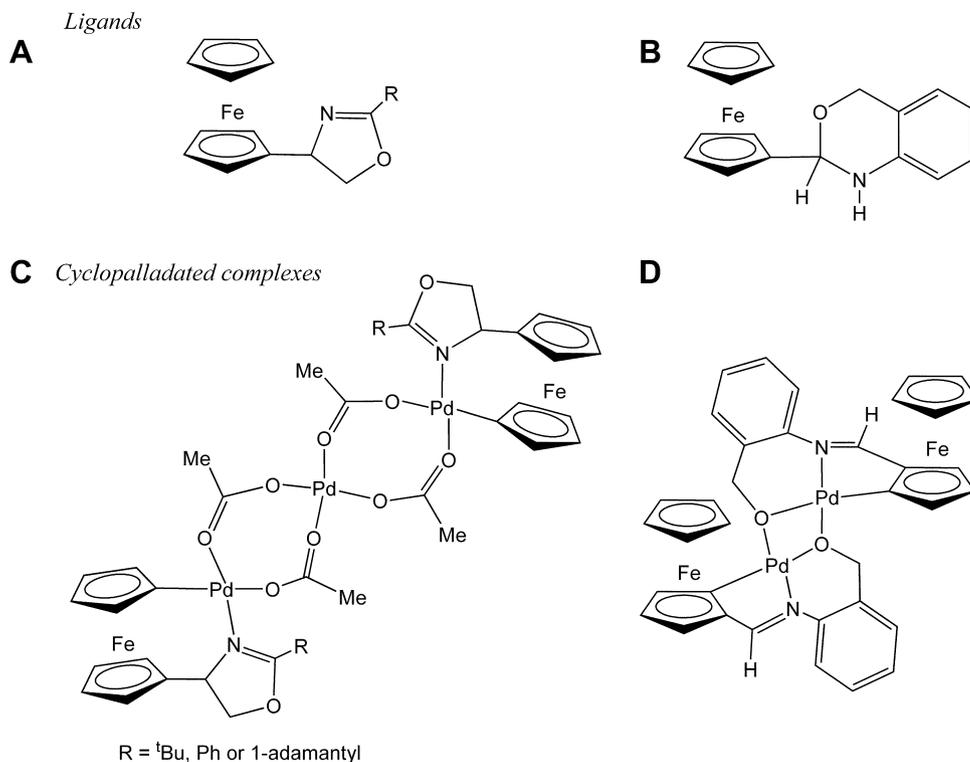


Fig. 1. Ferrocenyl ligands containing oxazoline and oxazine rings (A and B) used previously in the cyclopalladation reaction together with the chemical formulae of some of their palladated derivatives (C and D).

These transition metal complexes may also present interesting electrochemical properties. For instance, electrochemical studies of the tetrametallic complex $[\text{Pd}\{(\eta^5\text{-C}_5\text{H}_5)\text{-CH=N-(C}_6\text{H}_4\text{-2CH}_2\text{O)}\}]$ (Fig. 1D), formed by cyclopalladation of the 2-ferrocenyl-2,4-dihydro-1H-3,1-benzoxazine (Fig. 1B) have shown that the central “Pd(μ-O)₂Pd” moiety allows electronic communication between two iron(II) centres [6g]. However, and despite of the increasing interest on palladium(II) complexes with ligands containing simultaneously a ferrocenyl unit and a (N,O) or (N,S) heterocycle [6g,6h,6i,6j,9,10] parallel studies on related compounds with azole rings are scarce [6i,11] and only one of them refers to palladium(II) complexes containing simultaneously a bidentate [C,N(pyrazole)][−] ligand and a ferrocenyl unit [6i].

In view of these facts, we focused our attention on the synthesis of novel ferrocene derivatives containing pyrazolyl units and to study their reactivity towards transition metals. In this work, we present the syntheses and characterization of compounds $[\text{C}_6\text{H}_4\text{-4-R-1-}\{(3,5\text{-Me}_2\text{-C}_3\text{N}_2)\text{-CH}_2\text{-(}\eta^5\text{-C}_5\text{H}_4\text{)Fe(}\eta^5\text{-C}_5\text{H}_5\text{)}\}]$ (**1**) [with R = OMe (**1a**) or H (**1b**)] (Fig. 2), that contain a *N*-phenyl substituted

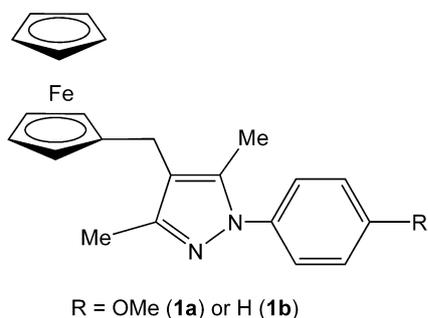


Fig. 2. New ferrocenyl ligands (**1a** and **1b**) containing pyrazolyl units under study.

pyrazolyl group in the pendant arm of the ferrocene. The study of their reactivity to palladium(II) acetate and a preliminary account of the reactivity of the palladium(II) complexes obtained with dimethyl acetylenedicarboxylate is also reported.

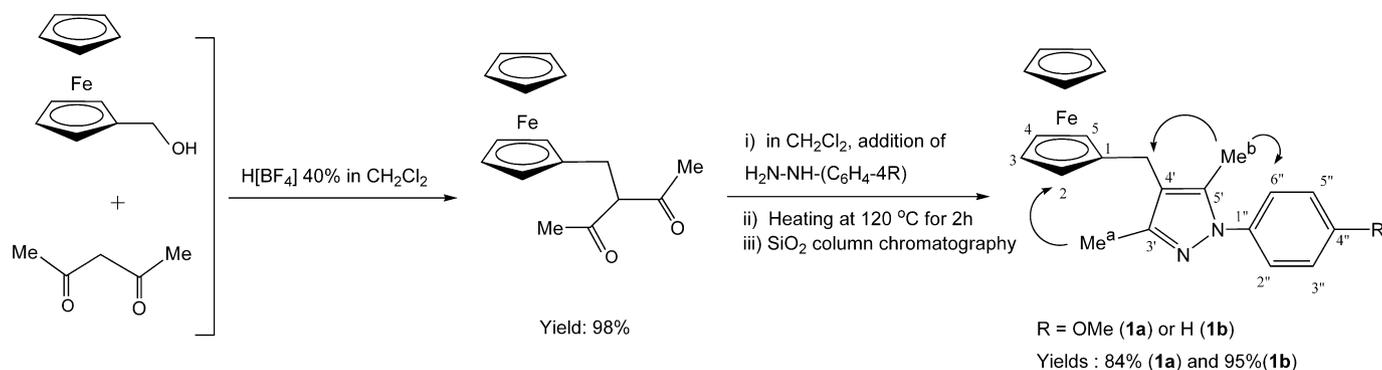
2. Results and discussion

2.1. The ligands

Compounds **1** were prepared from pentane-2,4-dione using a straightforward two-step procedure (Scheme 1). First, 3-ferrocenylmethyl-pentane-2,4-dione was obtained by electrophilic coupling on position 3 of the diketone using ferrocenylmethanol in a two-phase dichloromethane/40% aqueous tetrafluoroboric acid mixture [12]. Subsequent treatment with either 4-methoxyphenylhydrazine or phenylhydrazine at 120 °C [13] followed by the purification of the crude product of the reaction by column chromatography gave the pyrazole-containing ferrocenyl ligands in good yields [84% (for **1a**) and 95% (for **1b**)].

Ligands **1** were characterized by elemental analyses, mass spectrometry, infrared spectra and mono- and two-dimensional NMR experiments. The elemental analyses (Section 3) were consistent with the proposed formulae and their mass spectra showed a peak at $m/z = 401$ (for **1a**) or at 371 (for **1b**) that agree with the values expected for the cations $\{[M]+H\}^+$.

Proton-NMR spectra of **1** showed the typical pattern of mono-substituted ferrocene derivatives [6d,6g,14,15]. It consists of a group of three signals of relative intensities 5:2:2 in the range 4.00–4.20 ppm which are assigned to protons of the C₅H₅ moiety and to the pairs of protons (H² and H⁵) and (H³ and H⁴) of the other ring. The resonances arising from the methylenic protons appeared as a singlet at around 3.50 ppm. The two additional singlets, at 2.15 ppm < δ < 2.30 ppm, were assigned to methyl groups of the heterocycle. The singlet at higher fields showed NOE peaks with



Scheme 1.

those from the $-\text{CH}_2-$ unit and with the proton on the ortho site ($\text{H}^{6''}$) of the aromatic ring. This coupling is only possible for the methyl group bound to the $\text{C}^{5'}$ carbon of the pyrazolyl unit (Me^b). Two doublets and one triplet (for **1a**) or a triplet and a broad multiplet (for **1b**) arising from the protons of the phenyl ring were also observed in the low field region of the spectra. The resonance of the protons of the OMe unit of **1a** appeared as a singlet at 3.81 ppm.

The assignment of the signals observed in $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **1** (Section 3) was carried out with the aid of two-dimensional $\{^1\text{H}-^{13}\text{C}\}$ HSQC and HMBC experiments. The resonances corresponding to the quaternary carbon nuclei of **1** were easily detected by comparison of the signals detected in the $^{13}\text{C}\{^1\text{H}\}$ and in the HSQC spectra. The analyses of the cross-peaks, detected in the HMBC spectra, between the signal of the $-\text{CH}_2-$ protons allowed to assign the resonances of the *ipso* carbon of the ferrocenyl unit (C^1) and of the $\text{C}^{4'}$ nuclei. The singlet of the Me^b protons also showed two cross-peaks with the quaternary carbon atoms $\text{C}^{4'}$ (previously identified) and $\text{C}^{5'}$; while the Me^a protons correlated with the $\text{C}^{3'}$ and $\text{C}^{4'}$ atoms.

As a result of the increasing interest in the electrochemistry of organometallic compounds [16] and of ferrocene derivatives in

particular [6g,6h,14,16] we also undertook electrochemical studies on ligands **1**. Electrochemical data were obtained by cyclic voltammetric studies of freshly prepared solutions (10^{-3} M) in acetonitrile using $(\text{Bu}_4\text{N})[\text{PF}_6]$ as supporting electrolyte. The cyclic voltammograms of **1** (Fig. 3) showed an anodic peak with a directly associated reduction peak in the reverse scan and for the two ligands the positions of these peaks (Table 1) are very similar [the differences do not exceed 3σ ($\sigma = \pm 5$ mV)]. Since **1a** and **1b** differ in the nature of the substituent on the *meta*-position of the phenyl ring, which is far away from the ferrocenyl unit, the replacement of the OMe (in **1a**) by the hydrogen (in **1b**) is not expected to produce significant variations on the electronic environment of the iron(II). In both cases the ΔE parameter departs appreciably from the value of 59 mV (theoretically expected for a one electron-step oxidation–reduction process [17]), suggesting that a structural reorganization takes place on oxidation.

Previous electrochemical studies of ferrocene derivatives have shown that the presence of electron-withdrawing groups inhibits the oxidation of the iron(II) while the electron-donor substituents facilitate the oxidation [18,19]. For **1**, the position of the anodic peaks appears at slightly higher potentials than for ferrocene. This characteristic indicates that the substituent “ $\text{C}_6\text{H}_3-4\text{-R}-1-[(3,5\text{-Me}_2\text{-C}_3\text{N}_2)\text{-CH}_2\text{-}]$ ” is slightly more electron-donating than the hydrogen in ferrocene.

Another interesting feature arises from the comparison of the electrochemical behaviour of **1** and other ferrocene derivatives with azole groups, such as 4-ferrocenylpyrazol (**1c**) or 4-ferrocenyl-1-tritylpyrazol (**1d**), ferrocenyltriazole (**1e**), or ferrocenyltetrazole (**1f**), depicted in Fig. 4 [20a,20b]. The comparison of the half-wave potentials $\{E_{1/2}\}$ for **1a**, **1b**, **1c** ($E_{1/2} = -30$ mV [20a]) and **1d** ($E_{1/2} = -40$ mV [20a]) reveals that the incorporation of the $-\text{CH}_2-$ moiety between the ferrocenyl ligand and the pyrazole ring reduces the proclivity of the iron(II) to oxidize, but this effect is smaller than for the systems containing tri- or tetrazole units (**1c** and **1d**, with $E_{1/2} = 0.21$ and 0.27 V, respectively) [20b].

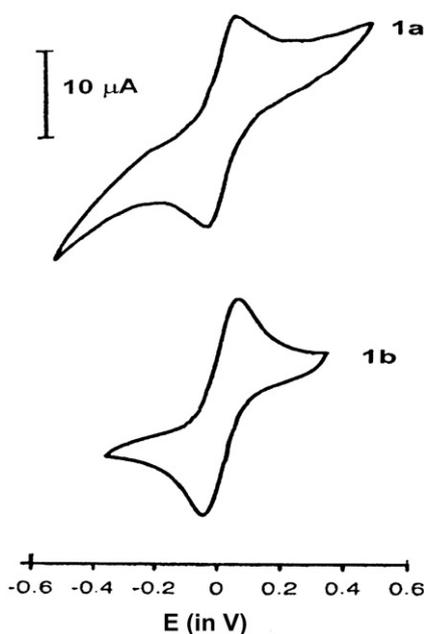


Fig. 3. Cyclic voltammograms of ligands **1a** and **1b** in acetonitrile at 298 K at a scan speed $\nu = 100$ mV/s.

Table 1

Summary of electrochemical data [anodic and cathodic potentials (E_{pa} and E_{pc} , respectively, referred to the ferrocene/ferricinium couple) and separation between peaks (ΔE) in mV] for ligands **1a** and **1b** and for their cyclopalladated complexes: $[\text{Pd}(\text{C}_6\text{H}_3-4\text{-R}-1-[(3,5\text{-Me}_2\text{-C}_3\text{N}_2)\text{-CH}_2\text{-}(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)])\text{Cl}(\text{PPh}_3)]$ (**6**) and $[\text{Pd}(\text{C}_6\text{H}_3-4\text{-R}-1-[(3,5\text{-Me}_2\text{-C}_3\text{N}_2)\text{-CH}_2\text{-}(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)])\text{Cl}(\text{acac})]$ (**7**)

Compound	R	E_{pa}	E_{pc}	ΔE
1a	OMe	30	-41	71
1b	H	34	-46	80
6a	OMe	132	22	110
6b	H	140	12	128
7a	OMe	163	64	99
7b	H	171	84	87

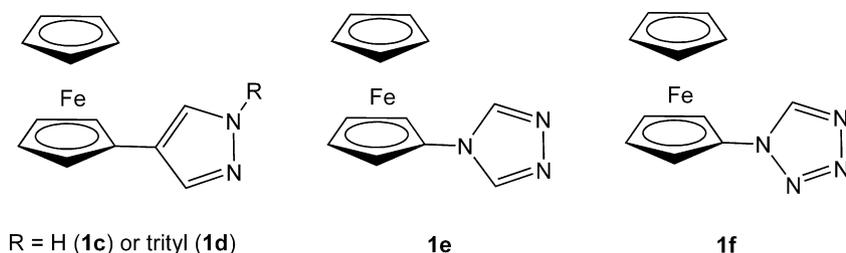


Fig. 4. Related ferrocenyl ligands containing azole units studied previously.

2.2. Palladium(II) compounds

In order to study the potential binding ability of ligands **1** towards palladium(II) their reactivity with Pd(AcO)₂ was studied under different experimental conditions. Treatment of **1** with the equimolar amount of Pd(AcO)₂ in a mixture of glacial acetic acid and acetic anhydride (5:1) under reflux for 3 h produced the formation of large amounts of metallic palladium and a nearly black solution. The subsequent concentration to dryness of the filtrate and the work up of a SiO₂ column gave small amounts of a bright yellow solid [hereafter referred to as **2a** or **2b** (for **1a** and **1b**, respectively)] (Scheme 2). Characterization data of **2** (Section 3) were consistent with those expected for the dimeric complexes: (μ-AcO)₂[Pd{κ²-C,N-C₆H₃-4-R-1-[(3,5-Me₂-C₃N₂)-CH₂-(η⁵-C₅H₄)-Fe(η⁵-C₅H₅)]}]₂ (**2**) [R = OMe (**2a**) or H (**2b**)] that arise from the metallation of the phenyl ring. Unfortunately, the yields of **2** were extremely low (20% for **2a** and 16% for **2b**) and clearly smaller than those reported by Mendoza et al. [11] for the cyclometallation of 3-

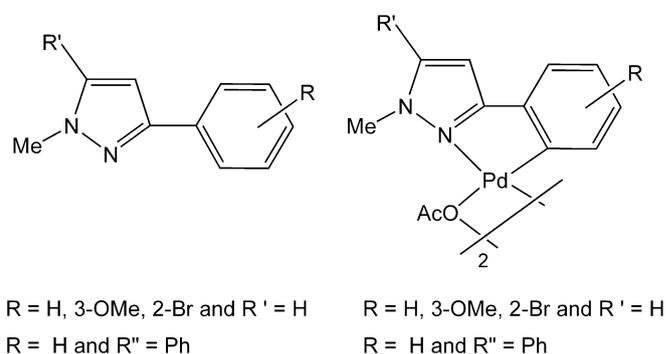
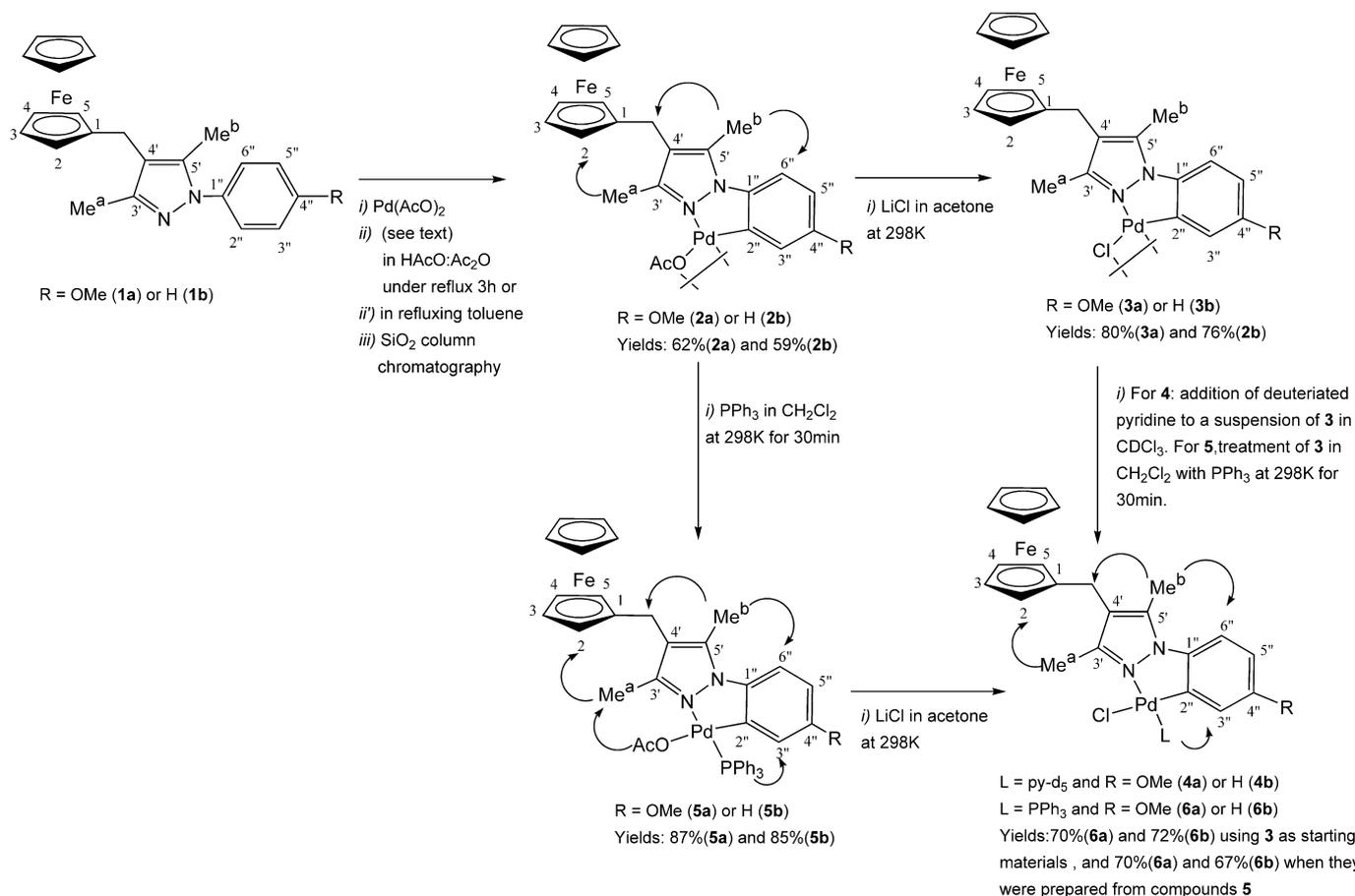


Fig. 5. Organic ligands containing pyrazolyl units described by Mendoza et al. [11] and their dinuclear cyclopalladated derivatives containing bridging acetato groups.

phenylpyrazole derivatives (Fig. 5) under identical experimental conditions.



Scheme 2.

More interesting were the results obtained when these reactions were performed using toluene as solvent (Scheme 2). In these cases, and after a similar work-up, compounds **2** were isolated in higher yields (ca. 60%). The comparison of the results obtained from the reactions presented in Scheme 2, indicates that the optimization of the synthetic method of **2** can be easily achieved by replacement of the mixture acetic acid/acetic anhydride (5:1) by toluene.

The infrared spectra of **2** showed two bands arising from the symmetric and asymmetric stretchings of the carboxylato groups at 1563 and 1431 cm^{-1} (for **1a**) or at 1576 and 1444 cm^{-1} (for **1b**). The separation between these two absorption bands suggested, according to the bibliography [21], that the AcO^- behaved as a (*O,O'*) bridging ligand.

It is well-known that the dimeric cyclopalladated complexes with acetato groups as bridging ligands may exhibit different isomeric forms [6f,22,23]. In these isomers, the two halves of the molecule could be in a *cis*- or *trans*-arrangement. It has been reported that for the *trans*-isomers the resonance of the methyl groups of the bridging ligands appear as one singlet [22,23]; but it splits into two singlets in the *cis*-isomers. The ^1H NMR spectra of **2** showed only one singlet [at 2.16 (for **2a**) or 2.14 ppm (for **2b**)], suggesting that in **2** the two halves are in a *trans*-arrangement. The high field shift of the resonance of the methylic protons Me^a of the pyrazolyl unit is also consistent with a *trans*-structure [22,23]. Most of the acetato-bridged cyclopalladated dimers described before show a folded structure (commonly known as *open-book* structure) in solution as well as in the solid state [22,23]. On this basis we assumed that in **2** the relative orientation of the acetato ligands corresponds to the *open-book* type with a C_2 symmetry.

The most relevant features detected in the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **2** were: (a) the absence of the signal ascribed to the proton $\text{H}^{2''}$ on the ortho site of the phenyl ring, (b) a high-field shift of

the resonances arising from the aromatic protons of ligands **1**, and (c) a significant decrease of the intensity of the resonance due to the carbon-13 nuclei on the ortho site of the phenyl ring ($\text{C}^{2''}$) and shifted downfield when compared with the free ligand. The observations are similar to those reported for other *N*-donor phenyl ligands and their cyclopalladated complexes with a $\sigma[\text{Pd}-\text{C}(\text{sp}^2, \text{phenyl})]$ bond [24]. Furthermore, $\{^1\text{H}-^{13}\text{C}\}$ HSQC NMR spectra of **2** showed only three (for **2a**) or four (for **2b**) cross peaks in the aromatic region, which is consistent with the metallation of the aromatic ring on position $2''$. The assignments of the signals of the protons and carbon nuclei of compounds **2a** and **2b** presented in Section 3 was carried out with the aid of the two dimensional experiments: $\{^1\text{H}-^1\text{H}\}$ NOESY and COSY and $\{^1\text{H}-^{13}\text{C}\}$ NOESY.

We also studied the reactivity of the cyclopalladated complexes with LiCl and triphenylphosphine (Scheme 2). The action of an excess of LiCl to acetone solutions of **2** at 298 K for 10 h produced yellow precipitates. These solids, that were identified as $(\mu\text{-Cl})_2[\text{Pd}\{\kappa^2\text{-C,N-C}_6\text{H}_3\text{-4-R-1-}[(3,5\text{-Me}_2\text{-C}_3\text{N}_2)\text{-CH}_2\text{-(}\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)]\}]_2$ (**3**) [R = OMe (**3a**) or H (**3b**)], arise from the substitution of the two bridging acetato units by the chloride ligands. Elemental analyses of **3** (Section 3) were consistent with those expected for the dimeric products $(\mu\text{-Cl})_2[\text{Pd}\{\kappa^2\text{-C,N-C}_6\text{H}_3\text{-4-R-1-}[(3,5\text{-Me}_2\text{-C}_3\text{N}_2)\text{-CH}_2\text{-(}\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)]\}]_2$ (**3**) [R = OMe (**3a**) or H (**3b**)]. Unfortunately, compounds **3** are extremely insoluble in the most common solvents used for NMR studies, and this precluded their characterization by NMR. However, the addition of a few drops of pyridine (py-d_5) to a suspension of **3a** or **3b** in CDCl_3 , produced the complete dissolution of the palladium(II) complex and the proton NMR spectra of the resulting bright yellow solutions suggested the presence of the monomeric derivatives $[\text{Pd}\{\kappa^2\text{-C,N-C}_6\text{H}_3\text{-4-R-1-}[(3,5\text{-Me}_2\text{-C}_3\text{N}_2)\text{-CH}_2\text{-(}\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)]\}\text{Cl}(\text{py-d}_5)]$ (**4**) [Scheme 2].

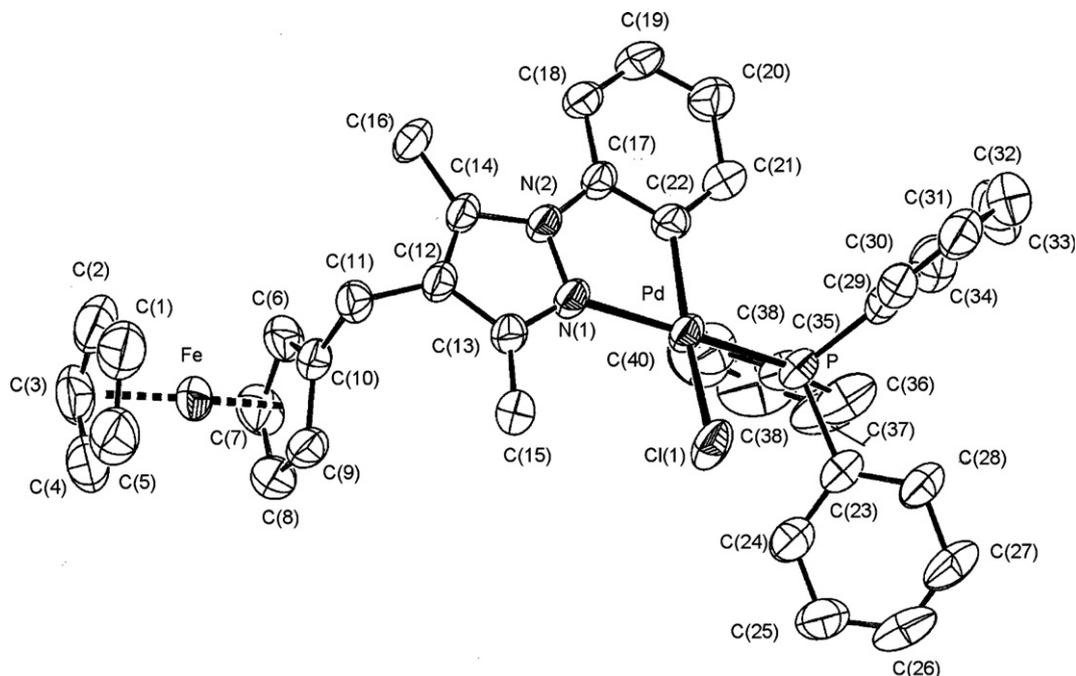


Fig. 6. ORTEP plot of the crystal structure of compound $[\text{Pd}\{\kappa^2\text{-C,N-C}_6\text{H}_3\text{-4-R-1-}[(3,5\text{-Me}_2\text{-C}_3\text{N}_2)\text{-CH}_2\text{-(}\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)]\}\text{Cl}(\text{PPh}_3)]$ (**6b**) $\cdot 1/2\text{CH}_2\text{Cl}_2$. The molecule of CH_2Cl_2 and hydrogen atoms have been omitted for clarity. Selected bond lengths (in Å) and angles (in $^\circ$): Pd–C(22), 2.035(5); Pd–N(1), 2.104(4); Pd–P, 2.2683(17); Pd–Cl(1), 2.389(2); C(10)–C(11), 1.504(6); C(11)–C(12), 1.507(5); N(1)–N(2), 1.401(4); N(1)–C(13), 1.331(5); C(12)–C(13), 1.416(6); C(12)–C(14), 1.381(6); C(14)–N(2), 1.376(5); N(2)–C(17), 1.394(5); C(17)–C(22), 1.406(6); C(17)–C(18), 1.394(5); C(18)–C(19), 1.378(6); C(19)–C(20), 1.384(7); C(20)–C(21), 1.407(6); C(21)–C(22), 1.359(6); N(1)–Pd–C(22), 79.68–(17); C(22)–Pd–P, 95.18(14); P–Pd–Cl(1), 89.64(8); Cl(1)–Pd–N(1), 97.25(12); C(10)–C(11)–C(12), 109.6(3); C(14)–C(12)–C(11), 126.5(4); C(13)–C(12)–C(11), 126.3(4); N(1)–C(13)–C(12), 109.4(4); N(1)–C(13)–C(15), 122.9(4); C(12)–C(13)–C(15), 127.7(4); N(2)–C(14)–C(12), 107.1(3); N(2)–C(14)–C(16), 124.3(4); C(12)–C(14)–C(16), 128.6(4); N(2)–C(17)–C(18), 121.1(4); N(2)–C(17)–C(22), 117.0(3); N(2)–N(1)–Pd, 112.6(3); C(14)–N(2)–N(1), 109.3(3); C(14)–N(2)–C(17), 134.5(3); N(2)–N(1)–C(13), 107.2(3).

The dinuclear complexes **2** and **3** reacted with triphenylphosphine [in a molar ratio PPh_3 : (**2** or **3**) = 2] in CH_2Cl_2 at 298 K giving the monomeric derivatives $[\text{Pd}\{\kappa^2\text{-C,N-C}_6\text{H}_3\text{-4-R-1-}[(3,5\text{-Me}_2\text{-C}_3\text{N}_2)\text{-CH}_2\text{-}(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)]\}\text{(X)(PPh}_3)]$ [$\text{X} = \text{AcO}^-$ (**5**) or Cl^- (**6**)] (Scheme 2). The formation of **4**, **5** and **6** requires the splitting of the central “ $\text{Pd}(\mu\text{-X})_2\text{Pd}$ ” units of **2** ($\text{X}^- = \text{AcO}^-$) or **3** ($\text{X}^- = \text{Cl}^-$) and the incorporation of a molecule of deuterated pyridine (in **4**) or of PPh_3 (in **5** and **6**) in the coordination sphere of the palladium(II). A metathesis reaction between **4** and LiCl in acetone at 298 K also gave products **6** (Scheme 2).

Compounds **5** and **6** were characterized by elemental analyses, mass and IR spectra and mono- $[\text{}^1\text{H}$, $^{13}\text{C}\{^1\text{H}\}]$ and $^{31}\text{P}\{^1\text{H}\}]$ and bidimensional NMR studies. Elemental analyses and mass spectra of **5**–**6** were consistent with the proposed formulae. The IR spectra of **5** and **6** showed the typical bands due to the coordinated PPh_3 ligands [21,25] and for **5** the difference between the position of the bands due to the symmetric and asymmetric stretching of the $>\text{CO}_2$ – unit agreed with the values reported for palladium(II) complexes with acetato group acting as a monodentate ligand [21]. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **5** and **6** showed a singlet in the range 44–45 ppm. The replacement of the acetato ligand (in **5a** or **5b**) by the chloro (in **6a** or **6b**) produces a small downfield shift of the signal [26]. The $\{^1\text{H}-^1\text{H}\}$ NOESY spectra of **5** and **6** showed the existence of a NOE peak between the resonance due to $\text{H}^{2''}$ and one aromatic proton of the phosphine. Besides that in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra the signal due to the metallated carbon ($\text{C}^{2''}$) appeared as a doublet due to phosphorus coupling. These results are indicative of

a *cis*-arrangement between the phosphorus and the metallated carbon ($\text{C}^{2''}$) in good agreement with the so-called transphobia effect [27].

In order to confirm the mode of binding of the ligand in the palladium(II) complexes a crystal of **6b** was grown. Unfortunately, the quality of the crystal was poor but attempts to isolate a better crystal using other precipitating agents or experimental conditions did not succeed.

The crystal structure contains molecules of $[\text{Pd}\{\kappa^2\text{-C,N-C}_6\text{H}_4\text{-1-}[(3,5\text{-Me}_2\text{-C}_3\text{N}_2)\text{-CH}_2\text{-}(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)]\}\text{Cl(PPh}_3)]$ (Fig. 6) and CH_2Cl_2 . In the heterodimetallic molecules the palladium is bound to the N(1) atom and the carbon {C(22)} on the ortho site of the phenyl ring. Thus, confirming a $[\text{C}(\text{sp}^2, \text{phenyl}), \text{N}]^-$ mode of binding of the ligand. The Pd–N(1) bond length [2.104(4) Å] is longer than the single bond predicted value of 2.011 Å and the Pd–C(22) bond distance [2.035(5) Å] falls in the range reported for related palladacycles containing bidentate $[\text{C}(\text{sp}^2, \text{phenyl}), \text{N}]^-$ ligands [11,22].

A chloride atom and the phosphorus of the PPh_3 ligand complete the coordination sphere of the metal which is in a slightly-distorted square-planar environment. The Pd–P and Pd–Cl bond distances [2.2683(17) Å and 2.389(2) Å, respectively] are similar to the values obtained for compounds of the type $[\text{Pd}\{\text{C}(\text{sp}^2, \text{phenyl}), \text{N}\}\text{Cl(PPh}_3)]$ [22,24,25]. The value of the P–Pd–C(22) angle [95.09(17)°] confirms a *cis*-arrangement between the metallated carbon and the phosphine ligand, in good agreement with the transphobia effect [27]. The angles between adjacent atoms in

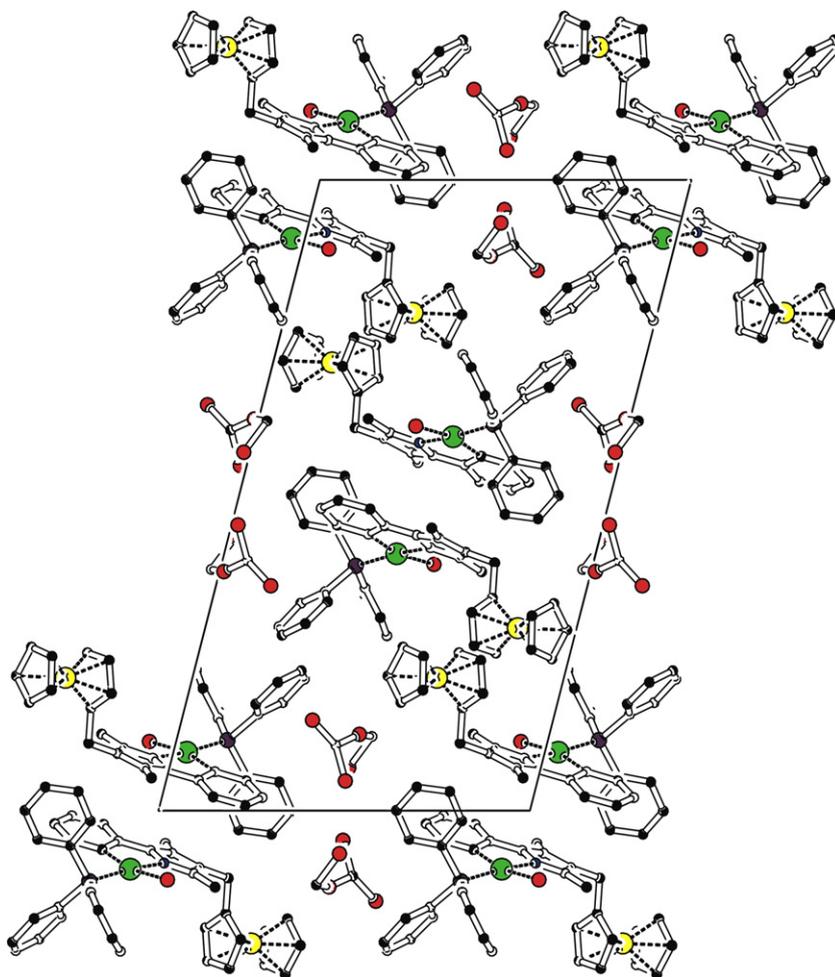


Fig. 7. Schematic view of the arrangement of the heterodimetallic molecules $[\text{Pd}\{\kappa^2\text{-C,N-C}_6\text{H}_3\text{-1-}[(3,5\text{-Me}_2\text{-C}_3\text{N}_2)\text{-CH}_2\text{-}(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)]\}\text{Cl(PPh}_3)]$ (**6b**) in the crystal. (Hydrogen atoms have been omitted for clarity).

the coordination sphere of palladium(II) lie in the range 79.68(17)–95.25(12)°, the smallest angle corresponding to the metallacycle and the largest to the N–Pd–Cl angle.

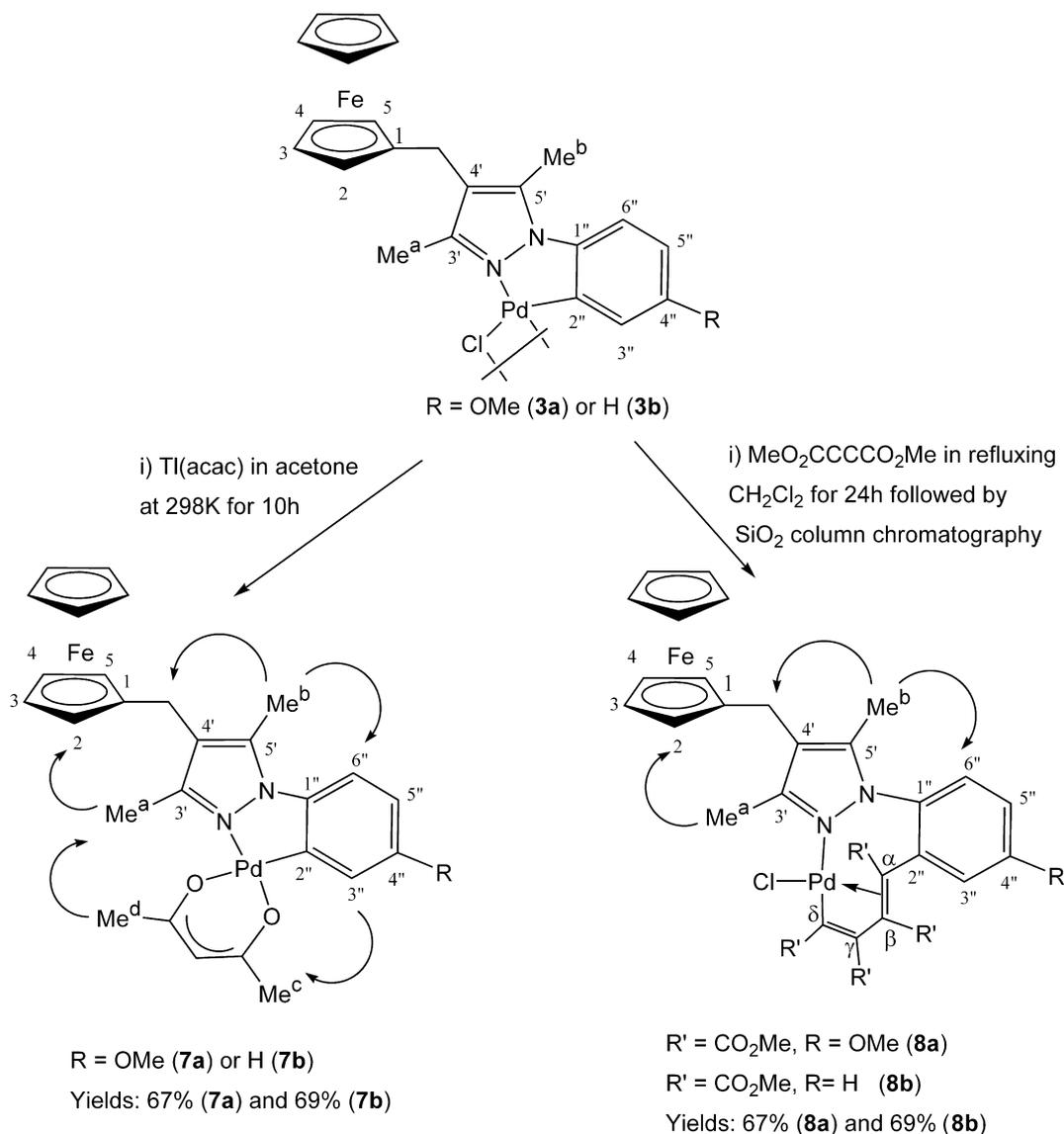
Each molecule contains a [5.5.6] tricyclic system formed by a five-membered palladacycle, the pyrazole ring and the phenyl group. The metallacycle, which is formed by the set of atoms [Pd, N(1), N(2), C(17) and C(18)], is practically planar and the distance between the palladium(II) and the iron(II) atoms (8.141 Å) excludes the existence of any direct interaction [28]. As expected bond lengths and angles of the two ferrocenyl units are consistent with the values reported for most ferrocene derivatives [22]. In both cases the pentagonal rings of the ferrocenyl unit are planar, practically parallel (*tilt angle* of 4.3°) and they deviate from the ideal eclipsed conformation by 2.1(4)°.

In the crystal, two vicinal molecules are associated in a *head to tail* arrangement and the separation between the phenyl ring of one of these units and the pyrazolyl group of the unit located at $(-x, 1-y, -z)$ is indicative of π -stacking of these cycles (Fig. 7). In addition, the distance between the chloride of one of these molecules and the hydrogen H(31) of the phosphine ligand of another molecule of a neighbouring couple (2.801 Å) equals the sum of the

van der Waals radii of these atoms (C, 1.70 and H, 1.10 Å [28]). This suggests a weak C–H...Cl interaction which connects the pairs forming a chain (Fig. 7).

The action of thallium(I) acetylacetonate upon acetone suspensions of **3** at 298 K produced the precipitation of thallium(I) chloride and the formation of a yellow solution which gave, after concentration, $[\text{Pd}\{\kappa^2\text{-C,N-C}_6\text{H}_3\text{-4-R-1-}[(3,5\text{-Me}_2\text{-C}_3\text{N}_2)\text{-CH}_2\text{-}(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)]\}\text{(acac)}]$ (**7**) [R = OMe (**7a**) or H (**7b**)] (Scheme 3). Characterization data of **7** (Section 3) agreed with the proposed formulae. Their IR spectra showed the typical bands due to the acetylacetonato(–1) ligand acting as a bidentate (O,O)– group [21]. The resonances of the methyl protons of the acac ligand (Me^c and Me^d) appeared as two singlets in the range 1.8–2.1 ppm and the analysis of cross-peaks detected in the ¹H–¹H NOESY spectra suggested that the signal at higher fields was due to the Me^c protons. The differences detected in the chemical shifts of the carbon nuclei of the two >CO units can be ascribed to the different *trans*-influence of the two donor atoms of the bidentate $[\text{C}(\text{sp}^2, \text{phenyl}), \text{N}]^-$ ligands [29].

In order to elucidate the effect produced by the coordination of the palladium(II) and the nature of the ligands bound to it upon the



Scheme 3.

electronic environment of the iron we also studied the electrochemical properties of a selection of the new cyclopalladated complexes using the same methodology as for the free ligands (see above and Section 3). Unfortunately, the instability of compounds **2** in acetonitrile [30] and the low solubility of the dimeric complexes **3** did not allow us to include these products in this study. In all the remaining cases the cyclic voltammograms showed one oxidation and one reduction peak. The electrochemical parameters presented in Table 1, show that the binding of the palladium(II) produces a slight decrease of the proclivity of the iron(II) to be oxidized when compared with that of the corresponding free ligand in good agreement with the results reported for related palladium(II) complexes containing N-donor ferrocenyl ligands [6g,6h,31]. Also in these cases the magnitude of the ΔE (>59 mV) suggests that a structural reorganization takes place on oxidation. The differences in the backbone of the ferrocenyl ligand do not affect significantly the electrochemical behaviour of the palladium(II) compounds. In addition, data of Table 1, reveals that the replacement of the two monodentate ligands (Cl^- and PPh_3) (in **6**) by the bidentate acetylacetonato(-1) ligand (in **7**) (Table 1 and Fig. 8) produces a slight shift (of ca. 30 mV) of the wave to the more anodic region. It should be noted that in the two pairs of compounds changes take place at a seven-bond length distance from the iron(II) and consequently the effect induced by the replacement of the ligands bound to the palladium(II) ion the Fe(II) ion is expected to be weak.

2.3. Study of the reactivity of the $\sigma(\text{Pd}-\text{C})$ bond of **3**

As mentioned above one of the main applications of palladacycles is their use as precursors in organic and organometallic synthesis [1a,1e,1f,1g,6b,6c,32]. Commonly in these processes the first step consists on the insertion of small molecules (i.e. CO, alkenes, alkynes or isonitriles) into the $\sigma(\text{Pd}-\text{C})$ bond [1a,1e,1f,1g,6b,6c,32]. In view of this fact and as a first attempt to evaluate the potential utility of the new cyclopalladated complexes prepared in this work as precursors in synthesis, we decided to study the reactivity of the di- μ -chloro derivatives (**3**) towards

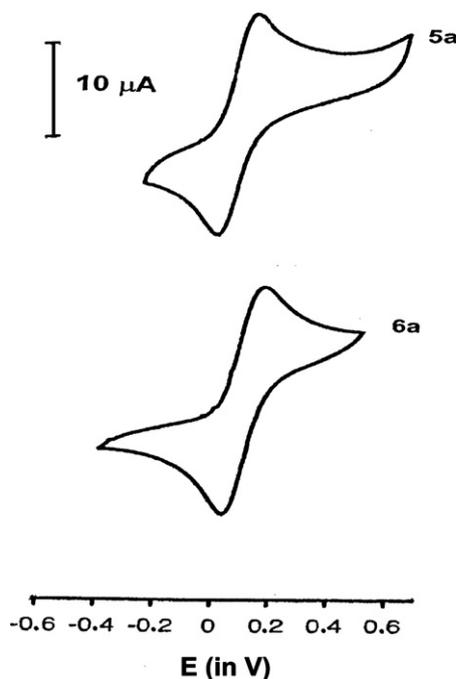


Fig. 8. Cyclic voltammograms of compounds **6a** and **7a** in acetonitrile at 298 K at a scan speed $\nu = 100$ mV/s.

dimethyl acetylenedicarboxylate. When suspensions of **3a** (or **3b**) in CH_2Cl_2 were treated separately with $\text{MeO}_2\text{C}-\text{C}\equiv\text{C}-\text{CO}_2\text{Me}$ (in a molar ratio alkyne: Pd(II) = 4) under reflux for 24 h a deep orange solution was formed (Scheme 3). Further evaporation of the solvent followed by a short SiO_2 -column chromatography using a CH_2Cl_2 :MeOH (100:0.1) mixture as eluant yield a yellow band that gave after concentration to dryness orange solids (**8**). These products, that were identified as $[\text{Pd}\{(\text{MeO}_2\text{C}-\text{C}\equiv\text{C}-\text{CO}_2\text{Me})_2(\text{C}_6\text{H}_3-4-\text{R}-1-[(3,5-\text{Me}_2-\text{C}_3\text{N}_2)-\text{CH}_2-(\eta^5-\text{C}_5\text{H}_4)\text{Fe}(\eta^5-\text{C}_5\text{H}_5)])\}\text{Cl}]$ (**8**) [R = OMe (**8a**) or H (**8b**), Scheme 3], arise from the bis(insertion) of the $\text{MeO}_2\text{C}-\text{C}\equiv\text{C}-\text{CO}_2\text{Me}$ into the $\sigma(\text{Pd}-\text{C}(\text{sp}^2, \text{phenyl}))$ bond of **3** and contain a [5.9.6] tricyclic system and a η^3 -butadienyl unit. Molar conductivities of 10^{-3} M solutions of **8** in acetone were consistent with the values expected for non-electrolytes [33]. The most relevant features observed in the ^1H NMR spectra of **8** is the presence of four singlets of identical intensity in the range: 3.0–4.0 ppm. In the HSQC spectra these signals showed cross-peaks with four singlets observed in the ^{13}C NMR spectra at $50 < \delta < 53$ ppm. In addition, the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra showed four singlets in the low-field region that are due to the carbon atoms of the COO units. The resonances of the central carbon of the inserted butadienyl unit $\text{C}^{\alpha}-\text{C}^{\beta}$ appeared at lower fields and exhibited low intensity. All these findings are similar to those reported for related palladacycles arising from the bis(insertion) of alkynes in which the two substituents close to the phenyl ring are in a *trans*-arrangement while the remaining two are on a *cis*-arrangement. This is the typical arrangement of groups found in the majority of palladacycles formed by a bis(insertion) process of alkynes into the $\sigma(\text{Pd}-\text{C})$ bond [34].

2.4. Conclusions

The studies presented here have allowed the isolation and characterization of two novel ferrocene derivatives containing pyrazolyl units. The study of their reactivity with $\text{Pd}(\text{AcO})_2$ has provided conclusive evidence of the advantages of the use of toluene as solvent to achieve the cyclopalladated products: $(\mu-\text{AcO})_2[\text{Pd}\{\kappa^2-\text{C},\text{N}-\text{C}_6\text{H}_3-4-\text{R}-1-[(3,5-\text{Me}_2-\text{C}_3\text{N}_2)-\text{CH}_2-(\eta^5-\text{C}_5\text{H}_4)\text{Fe}(\eta^5-\text{C}_5\text{H}_5)])\}_2$ (**2**). These compounds were easily transformed into the dimeric derivative $(\mu-\text{Cl})_2[\text{Pd}\{\kappa^2-\text{C},\text{N}-\text{C}_6\text{H}_3-4-\text{R}-1-[(3,5-\text{Me}_2-\text{C}_3\text{N}_2)-\text{CH}_2-(\eta^5-\text{C}_5\text{H}_4)\text{Fe}(\eta^5-\text{C}_5\text{H}_5)])\}_2$ (**3**) or the mononuclear complexes $[\text{Pd}\{\kappa^2-\text{C},\text{N}-\text{C}_6\text{H}_3-4-\text{R}-1-[(3,5-\text{Me}_2-\text{C}_3\text{N}_2)-\text{CH}_2-(\eta^5-\text{C}_5\text{H}_4)\text{Fe}(\eta^5-\text{C}_5\text{H}_5)]\}X(\text{PPh}_3)]$ [$X^- = \text{AcO}^-$ (**5**) or Cl^- (**6**)] and $[\text{Pd}\{\kappa^2-\text{C},\text{N}-\text{C}_6\text{H}_3-4-\text{R}-1-[(3,5-\text{Me}_2-\text{C}_3\text{N}_2)-\text{CH}_2-(\eta^5-\text{C}_5\text{H}_4)\text{Fe}(\eta^5-\text{C}_5\text{H}_5)]\}(\text{acac})]$ (**7**).

Electrochemical studies of the ligands as well as of the selected cyclopalladated compounds have shown that in all the new products the iron(II) is less prone to oxidation than in ferrocene, and the proclivity to be oxidized increases according to the sequence $7 \leq 6 < 1$. Besides that, for **1**, **6** and **7**, the change of the nature of the substituent (OMe or H) on the phenyl ring does not introduce significant variations in the electrochemical behaviour of these products.

The reactions of **3** with $\text{MeO}_2\text{C}-\text{C}\equiv\text{C}-\text{CO}_2\text{Me}$ lead the neutral palladacycles: $[\text{Pd}\{(\text{MeO}_2\text{C}-\text{C}\equiv\text{C}-\text{CO}_2\text{Me})_2-\text{C}_6\text{H}_3-4-\text{R}-1-[(3,5-\text{Me}_2-\text{C}_3\text{N}_2)-\text{CH}_2-(\eta^5-\text{C}_5\text{H}_4)\text{Fe}(\eta^5-\text{C}_5\text{H}_5)]\}\text{Cl}]$ (**8**) that contain a nine-membered ring formed by the bis(insertion) of the alkyne into the $\sigma(\text{Pd}-\text{C})$ bond indicating a high reactivity of this bond. Despite the large amount of papers centred on the study of the reactivity of palladacycles containing bidentate (C,N) $^-$ ligands in none of the examples reported so far the nitrogen atom belongs to an azole ring. Thus, the results presented here constitute the first step for further work on this field mainly centred on the insertion of other molecules (i.e. alkynes, alkenes, isonitriles, etc.) into the $\sigma(\text{Pd}-\text{C})$ bond. In addition, since it is well-known that palladacycles arising from the insertion of alkynes into the $\sigma(\text{Pd}-\text{C})$ bond may undergo depalladation reactions to give new organic compounds (i.e. func-

tionalized heterocycles) [1e,1f,1g,6b], compounds **8** described here appear to be excellent candidates to be studied in this field.

3. Experimental

3.1. Materials and methods

Acetylacetone, ferrocenylmethanol, 4-methoxyphenylhydrazine and phenylhydrazine, triphenylphosphine, HBF₄, Pd(AcO)₂, LiCl, and thallium(I) acetylacetonate were obtained from commercial sources and used as received. Solvents were distilled and dried before use [35]. Some of the preparations require the use of thallium(I) salts that should be handled with CAUTION!

Elemental analyses were carried out at the Serveis de Recursos Científics i Tècnics (Universitat Rovira i Virgili). Mass spectra (ESI⁺) were performed at the Servei d'Espectrometria de Masses (Universitat de Barcelona). Infrared spectra were obtained with a Nicolet 400FTIR instrument using NaCl discs (for the 3-ferrocenylmethyl-pentane 2,4-dione) and KBr pellets for the remaining compounds. Routine ¹H and ¹³C{¹H} NMR spectra were recorded with a Gemini-200 MHz or a Mercury-400 MHz instruments, respectively. ³¹P{¹H} NMR of **5** and **6** were recorded with a Varian-Unity-300 instrument using P(OMe₃) as reference [δ (³¹P) = 140.17 ppm]. High resolution ¹H NMR spectra and the two-dimensional [¹H–¹H] NOESY, [¹H–¹³C] HSQC and HMBC were registered with a Varian VRX-500 or a Bruker Avance DMX-500 MHz instruments at 298 K. The chemical shifts (δ) are given in ppm and the coupling constants (*J*) in Hz. The solvent for the NMR experiments was CDCl₃ (99.9%) and SiMe₄ was used as reference. Molar conductivity measurements of 10^{−3} M solutions of compounds **8** in acetone were determined at 298 K with a Crison microMC2200 conductivity-meter.

3.2. Synthesis of the compounds

3.2.1. 3-Ferrocenylmethyl-pentane 2,4-dione

To a solution of pentane-2,4-dione (0.272 g, 2.72 × 10^{−3} mol) and ferrocenylmethanol (0.588 g, 2.72 × 10^{−3} mol) in 25 mL of CH₂Cl₂, HBF₄ [40% in water (10 mL)] was added dropwise. Once the addition had finished the reaction mixture was stirred at room temperature for 1 h, diluted with water 40 mL and then extracted with 15 mL of CH₂Cl₂. The organic layer was dried over Na₂SO₄, filtered and concentrated in vacuo. The resulting oil (0.792 g, 98%) was characterized by mass spectra (ESI⁺), IR and NMR and used in the next step without further purification. *Characterization data*: MS (ESI⁺): 299 {[M]+H}⁺. IR: 3092(m), 3000(m), 2956(m), 2924(m), 1724(s), 1701(s), 1421(m), 1357(m), 1254(m), 1186(m), 1149(m), 1039(m), 1023(m), 1001(m), 821(s), and 618(m) cm^{−1}. ¹H NMR data [36]: δ = 4.12 (s, 5H, C₅H₅), 4.06 (s, 2H, H² and H⁵), 4.03 (s, 2H, H³ and H⁴), 3.79 (t, 1H, *J* = 7.2, >CH–), 2.89 (d, 2H, *J* = 7.2, –CH₂–) and 2.12 (s, 6H, Me^a and Me^b). ¹³C{¹H} NMR data: δ = 203 (>CO), 84.8 (C¹), 70.79 (>CH–), 68.8 (C₅H₅), 68.5 (C² and C⁵), 67.9 (C³ and C⁴) and 29.8 and 29.0 (Me^a and Me^b).

3.2.2. [C₆H₄-4-R-1-((3,5-Me₂-C₃N₂)-CH₂-(η^5 -C₅H₄)Fe(η^5 -C₅H₅))] [R = OMe (**1a**) or H (**1b**)]

For R = 4-OMe (**1a**): 4-methoxyphenylhydrazine (0.469 g, 3.39 × 10^{−3} mol) dissolved in 5 mL of CH₂Cl₂ was added to 3-ferrocenylmethyl-pentane-2,4-dione (1.02 g, 3.39 × 10^{−3} mol) and the solvent was evaporated under reduced pressure. The mixture was then heated for 2 h at 120 °C and cooled. The crude was taken up in CH₂Cl₂ and chromatographed on silica gel using diethylether as eluant. The band released was collected and concentrated to dryness giving a yellowish oily residue [yield: 1.222 g (84%)].

Ligand **1b** was synthesized following the same procedure but using phenylhydrazine (0.287 g, 2.65 × 10^{−3} mol) and the equimo-

lar amount of 3-ferrocenylmethyl-pentane-2,4-dione (0.792 g) [yield: 0.953 g (95%)].

Compounds **1** were recrystallized as follows: a 200 mg amount of **1** was dissolved in methanol (ca. 25 mL) and filtered out. Slow evaporation of the bright yellow solution at 298 K produced the precipitation of the desired product that was collected and air-dried.

Characterization data for 1a: Anal. Calc. for C₂₃H₂₄N₂OFe: C, 69.01; H, 6.04; N, 7.00. Found C, 68.87; H, 6.12; N, 6.88%. MS (ESI⁺): 401{[M]+H}⁺. IR: 3080(m), 2910(m), 1588(s), 1516(s), 1248(s), 1176(m), 1022(m), 835(s), 813(s), 608(m), 478(m) cm^{−1}. ¹H NMR data [36]: δ = 7.24 (d, 2H, *J* = 8.0, H^{2''} and H^{6''}), 6.91 (d, 2H, *J* = 8.0, H^{3''} and H^{5''}), 4.12 (s, 5H, C₅H₅), 4.09 (s, 2H, H² and H⁵), 4.03 (s, 2H, H³ and H⁴), 3.46 (s, 2H, –CH₂–), 3.81 (s, 3H, OMe), 2.25 (s, 3H, Me^a) and 2.16 (s, 3H, Me^b). ¹³C{¹H} NMR data [36]: δ = 158.5 (C^{4''}), 146.9 (C^{3''}), 135.9 (C^{5''}), 133.2 (C^{1''}), 126.0 (C^{2''} and C^{6''}), 117.6 (C^{4'}), 113.9 (C^{3'} and C^{5'}), 88.4 (C¹), 68.4 (C² and C⁵), 68.3 (C₅H₅), 67.9 (C³ and C⁴), 23.9 (–CH₂–), 11.9 (Me^b) and 10.7 (Me^a). For **1b**: Anal. Calc. for C₂₂H₂₂N₂Fe: C, 71.36; H, 5.99; N, 7.57. Found: C, 71.01; H, 6.05; N, 7.42%. MS (ESI⁺): 371 [M+H]⁺. IR: 3067(m), 2909(m), 2839(m), 1596(m), 1504(s), 1430(m), 1384(m), 1105(m), 1020(m), 817(s), 694(s) and 478(m) cm^{−1}. ¹H NMR data [36]: δ = 7.35–7.41 (m, 4H, H²–H^{6''}), 7.30 (td, 1H, *J* = 7.5 and 2.0, H^{4''}), 4.13 (s, 5H, C₅H₅), 4.11 (t, 2H, *J* = 1.5, H² and H⁵), 4.04 (t, 2H, *J* = 1.5, H³ and H⁴), 3.47 (s, 2H, –CH₂–), 2.23 (s, 3H, Me^a) and 2.26 (s, 3H, Me^b) and ¹³C{¹H} NMR data [36]: δ = 147.8 (C^{3'}), 140.0 (C^{1''}), 136.1 (C^{5'}), 128.8 (C^{2''} and C^{6''}), 126.9 (C^{4''}), 124.8 (C^{3''} and C^{5''}), 121.9 (C^{4'}), 88.4 (C¹), 68.5 (C₅H₅), 68.4 (C² and C⁵), 67.2 (C³ and C⁴), 24.3 (–CH₂–), 12.2 (Me^a) and 11.1 (Me^b).

3.2.3. (μ -AcO)₂[Pd{ κ^2 -C,N-C₆H₃-4-R-1-((3,5-Me₂-C₃N₂)-CH₂-(η^5 -C₅H₄)Fe(η^5 -C₅H₅))]]₂ (2) [R = OMe (**2a**) or H (**2b**)]

A 6.8 × 10^{−4} mol amount of **1a** (271 mg) or **1b** (251 mg) was dissolved in 10 mL of toluene. Then, a solution containing 152 mg (6.8 × 10^{−4} mol) of Pd(AcO)₂ and 10 mL of toluene was added. The reaction mixture was protected from the light with aluminium foil and refluxed for 3.5 h. During the reflux the deposition of metallic palladium on the walls of the flask was detected. After this period the resulting hot solution was filtered through a small plug (2.0 cm × 3.5 cm) of Celite. The bright yellow solution was concentrated to dryness and kept for further use. The Celite was allowed to dry overnight and then washed with CH₂Cl₂ until nearly colourless washings were obtained. The washings were poured into the flask containing the residue and then the resulting solution was concentrated to ca. 10 mL on a rotary evaporator and passed through a SiO₂ column (5.0 cm × 3.5 cm). Elution with a CH₂Cl₂/MeOH (100:0.4) solution produced the release of a wide and bright yellow band that was collected and concentrated to dryness on a rotary evaporator. The solid isolated were collected and dried in vacuum for 2 days [Yields: 236 mg (62%) and 212 mg (59%) for **2a** and **2b**, respectively]. *Characterization data for 2a*: Anal. Calc. for C₅₀H₅₂N₄Fe₂O₆Pd₂: C, 53.17; H, 4.64; N, 4.96. Found: C, 52.91; H, 4.53; N, 5.06%. MS (ESI⁺): MS (ESI⁺): 1082.1 {[M]–AcO[−]]⁺ and 517.5 {[M]–2AcO[−]]²⁺}/2. IR-data: 3066(m), 2909(m), 1591(s), 1568(s), 1483(m), 1431(m), 1410(s), 1282(m), 1262(m), 1224(m), 1211(m), 1104(m), 1038(m), 795(s), 684(m) and 482(m) cm^{−1}. ¹H NMR data [36]: δ = 7.10 (dd, 2H, *J* = 7.5 and 2.0, 2 H^{6''}), 6.59 (td, 2H, *J* = 7.5 and 2.0, 2H^{5''}), 6.40 (dd, 2H, *J* = 7.5 and 2.0, 2H^{3''}), 4.12 (s, 10H, 2C₅H₅), 4.01 (d, 4H, *J* = 1.5, 2H² and 2H⁵), 3.90 (t, 2H, *J* = 1.5, 2H³ and 2H⁴), 3.77 (s, 6H, 2 OMe), 3.10 (s, 4H, 2-CH₂–), 2.21 (s, 3H, 2Me^b), 2.16 [s, 6H, 2Me(AcO)] and 1.80 (s, 3H, 2Me^a). ¹³C{¹H} NMR data [36]: δ = 181.0 (>COO(AcO)), 157.4 (C^{4''}), 154.1 (C^{3''}), 149.4 (C^{2''}), 138.3 (C^{1''}), 134.4 (C^{6''}), 134.3 (C^{5''}), 117.9 (C^{4'}), 112.2 (C^{5''}), 109.5 (C^{3''}), 87.3 (C¹), 68.9 (C₅H₅), 68.5 (C⁵), 68.3 (C²), 67.5 (C³ and C⁴), 55.5 (OMe), 24.5 (–CH₂–), 23.1

[Me(AcO)], 12.1 (Me^a) and 11.0 (Me^b). For **2b**: Anal. Calc. for C₄₈H₄₈N₄Fe₂O₄Pd₂: C, 54.07; H, 4.52; N, 5.24. Found: C, 53.91; H, 4.70; N, 5.19%. 1022.1 {[M]–AcO[−]}⁺ and 486.1 {[M]–2AcO[−]}²⁺/2. IR-data: 3072(m), 2920(m), 2906(m), 1588(s), 1576(s), 1563(s), 1480(m), 1444(s), 1392(s), 1030(m), 815(m), 744(m), 495(m) and 482(m) cm^{−1}. ¹H NMR data [36]: δ = 6.92 (dd, 2H, J = 7.5 and 2, 2H^{6v}), 6.82 (td, 2H, J = 7.5 and 2.0, H^{5v}), 6.63 (td, 2H, J = 7.5 and 2.0, H^{4v}), 6.60 (dd, 2H, J = 7.5 and 2.0, 2H^{3v}), 4.08 (s, 10H, 2C₅H₅), 4.05 (d, 4H, J = 1.5, 2H² and 2H⁵), 3.90 (t, 4H, J = 1.5, 2H³ and 2H⁴), 3.07 (–CH₂–), 2.26 (s, 3H, 2Me^b), 2.14 [s, 6H, 2Me(AcO)] and 1.77 (s, 3H, 2Me^a). ¹³C{¹H} NMR data [36]: δ = 182.3 [C(=O)O(AcO)], 151.8 (C^{3v}), 140.8 (C^{2v}), 139.7 (C^{1v}), 136.1 (C^{5v}), 132.4 (C^{6v}), 124.0 (C^{5v}), 122.5 (C^{4v}), 118.8 (C^{4v}), 109.2 (C^{3v}), 87.7 (C¹), 68.8 (C₅H₅), 68.4 (C² and C⁵), 67.6 (C³ and C⁴), 24.1 [Me(AcO)], 23.5 (–CH₂–), 11.6 (Me^a) and 11.2 (Me^b).

3.2.4. (μ-Cl)₂[Pd{κ²-C,N-C₆H₃-4-R-1-[(3,5-Me₂-C₃N₂)-CH₂-(η⁵-C₅H₄)Fe(η⁵-C₅H₅)]₂] (**3**) [R = OMe (**3a**) or H (**3b**)]

A 90 mg (7.96 × 10^{−5} mol) amount of **2a** or the equimolar amount of **2b** (85 mg) was suspended in 30 mL of acetone, then LiCl (10 mg, 2.38 × 10^{−4} mol) was added. The resulting suspension was stirred for 12 h at 298 K. The solid formed was filtered out, air-dried and then dried in vacuum for 1 day [yields: 69 mg (80%) and 62 mg (76%) for **3a** and **3b**, respectively]. Characterization data for **3a**: Anal. Calc. for C₄₆H₄₆Cl₂N₄Fe₂O₂Pd₂: C, 51.05; H, 4.28; N, 5.18. Found: C, 49.74; H, 4.35; N, 4.87%. MS (ESI⁺): m/z = 1047.0 [M–Cl]⁺ and 506.0 {[M–2Cl]²⁺}/2. IR-data: 3071(m), 2918(m), 1484(s), 1420(s), 1284(m), 1216(m), 1040(s), 728(m), 526(m) and 478(m) cm^{−1}. For **3b**: Anal. Calc. for C₄₄H₄₂Cl₂N₄Fe₂Pd₂: C, 51.70; H, 4.14; N, 5.48. Found: C, 51.89; H, 4.20; N, 5.34%. MS (ESI⁺): m/z = 987.0 [M–Cl]⁺ and 475.0 {[M–2Cl]²⁺}/2. IR-data: 3061(m), 2915(m), 1484(s), 1399(s), 1275(m), 815(m), 744(s), 495(m) and 482(m) cm^{−1}.

3.2.5. [Pd{κ²-C,N-C₆H₃-4-R-1-[(3,5-Me₂-C₃N₂)-CH₂-(η⁵-C₅H₄)Fe(η⁵-C₅H₅)]Cl(py-d₅)] (**4**) [R = OMe (**4a**) or H (**4b**)]

These products were prepared in a NMR scale and characterized in solution by ¹H NMR. A 2.0 × 10^{−4} mol amount of the corresponding di-μ-chloro-bridged complex **3** (21 mg of **3a** or 22 mg of **3b**) was introduced in a NMR tube, then 0.7 mL of CDCl₃ were added. The resulting suspension was then treated with three drops of deuterated pyridine (py-d₅) and shaken for 2 min. This produced a bright yellow solution that contained the corresponding complex **4a** or **4b**. ¹H NMR data for **4a** [36]: δ = 7.13 (dd, 1H, H^{6v}), 6.58 (dd, 2H, J = 7.5 and 2.0, H^{5v}), 5.54 (s, 1H, H^{3v}), 4.14 (s, 5H, C₅H₅), 4.06 (br, 2H, H² and H⁵), 4.04 (br, 2H, H³ and H⁵), 3.58 (s, 3H, OMe), 3.49 (s, 2H, –CH₂–), 2.77 (s, 3H, 2Me^a) and 2.56 (s, 3H, 2Me^b). ¹³C{¹H} NMR data for **4a** [36]: δ = 155.2 (C^{4v}), 152.6 (C^{3v}), 147.3 (C^{2v}), 138.3 (C^{1v}), 136.2 (C^{6v}), 135.9 (C^{5v}), 112.6 (C^{5v}), 119.9 (C^{4v}), 108.7 (C^{3v}), 87.6 (C¹), 68.9 (C₅H₅), 68.4 (C² and C⁵), 67.7 (C³ and C⁴), 23.7 (–CH₂–), 13.7 (Me^a) and 12.8 (Me^b). ¹H NMR data for **4b** [36]: δ = 7.21 (dd, J = 7.0 and 1.5, 1H, H^{6v}), 7.06 (td, 2H, J = 7.0 and 1.5, H^{4v}), 6.71 (td, 2H, J = 7.0 and 1.5, H^{5v}), 6.07 (dd, 1H, H^{3v}), 4.14 (s, 5H, C₅H₅), 4.06 (s, 2H, H² and H⁵), 4.03 (s, 2H, H³ and H⁴), 3.48 (s, 2H, –CH₂–), 2.78 (s, 3H, 2Me^a) and 2.60 (s, 3H, 2Me^b). ¹³C{¹H} NMR data for **4b** [36]: δ = 158.4 (C^{3v}), 153.5 (C^{3v}), 145.2 (C^{2v}), 137.0 (C^{1v}), 133.4 (C^{5v}), 130.5 (C^{6v}), 125.2 (C^{5v}), 112.4 (C^{4v}), 112.2 (C^{4v}), 87.6 (C¹), 68.9 (C₅H₅), 68.4 (C² and C⁵), 67.5 (C³ and C⁴), 23.6 (–CH₂–), 13.8 (Me^a) and 13.1 (Me^b).

3.2.6. [Pd{κ²-C,N-C₆H₃-4-R-1-[(3,5-Me₂-C₃N₂)-CH₂-(η⁵-C₅H₄)Fe(η⁵-C₅H₅)](AcO)(PPh₃)] (**5**) [R = OMe (**5a**) or H (**5b**)]

Compound **2a** (70 mg, 6.2 × 10^{−5} mol) or **2b** (65 mg, 6.1 × 10^{−5} mol) or was dissolved in 20 mL of CH₂Cl₂, then PPh₃ [33 mg (12.6 × 10^{−5} mol) for **5a** or 32 mg (12.2 × 10^{−5} mol) for **5b**] was added. The reaction mixture was stirred at 298 K for 20 min and fil-

tered out. The filtrate was then concentrated to dryness on a rotary evaporator giving **5a** and **5b** as yellowish solid, that were collected and dried in vacuum for 5 h. [Yields: 89 mg (87%) and 82 mg (85%) and for **5a** and **5b**, respectively]. Characterization data for **5a**: Anal. Calc. for C₄₃H₄₁N₂FeO₃Pd: C, 62.45; H, 5.00; N, 3.39. Found: C, 62.0; H, 5.18; N, 3.18%. MS(ESI⁺): 767{[M]–AcO}⁺. IR-data: 3076(m), 3048(m), 2966(m), 2931(m), 1578(s), 1480(s), 1434(s), 1384(s), 1322(m), 1224(m), 1095(m) 721(s), 694(s), 542(s), 534(s), 511(m) and 498(m) cm^{−1}. ¹H NMR data [36]: δ = 7.10 (dd, 1H, J = 7.5 and 2.0, H^{6v}), 6.60 (dd, 1H, J = 7.5 and 2.0, H^{3v}), 6.41 (td, 1H, J = 7.5 and 2.0, H^{5v}), 4.13 (s, 5H, C₅H₅), 4.06 (s, 2H, H² and H⁵), 4.03 (s, 2H, H³ and H⁴), 3.48 (s, 2H, –CH₂–), 2.87 (s, 3H, OMe), 2.55 (s, 3H, 2Me^a), 2.39 (s, 3H, 2Me^b) and 1.24 [s, 3H, Me(AcO)]. ¹³C{¹H} NMR data [36]: δ = 181.4 [C(=O)O(AcO)], 158.4 (C^{3v}), 154.0 (C^{3v}), 149.3 (d, ²J_{P–C} = 10.6 C^{2v}), 138.2 (C^{1v}), 136.5 (C^{5v}), 135.1, 131.2, 129.3 and 128.2 (d, aromatic ¹³C nuclei of the PPh₃ ligand), 130.5 (C^{6v}), 117.9 (C^{4v}), 117.4 (C^{5v}), 111.2 (C^{4v}), 87.7 (C¹), 68.9 (C₅H₅), 68.4 (C² and C⁵), 67.5 (C³ and C⁴), 55.0 (OMe), 23.6 (–CH₂–), 23.4 [Me(AcO)], 13.8 (Me^a) and 13.2 (Me^b). ³¹P{¹H} NMR data: 44.6. For **5b**: Anal. Calc. for C₄₂H₃₉N₂FeO₂Pd: C, 63.29; H, 4.93; N, 3.51. Found: C, 63.32; H, 5.10; N, 3.44%. MS (ESI⁺): 737 {[M]–AcO}⁺. IR data: 3073(m), 3042(m), 2917(m), 2847(m), 1476(s), 1435(s), 1382(s), 1366(s), 1094(m), 1020(m), 894(m), 743(s), 691(s), 532(m), 512(m) and 496(m) cm^{−1}. ¹H NMR data [36]: δ = 7.20 (dd, 1H, J = 7.5 and 2, H^{6v}), 6.83 (td, 2H, J = 7.5 and 2, H^{4v}), 6.52 (dd, 2H, J_{P–H} = 6.5 and J_{H–H} = 2.0, H^{3v}), 6.28 (td, 2H, J = 7.5 and 2, H^{4v}), 4.14 (s, 5H, C₅H₅), 4.07 (s, 2H, H² and H⁵), 4.02 (s, 2H, H³ and H⁴), 3.42 (s, 2H, –CH₂–), 2.52 (s, 3H, 2Me^a), 2.33 (s, 3H, 2Me^b), and 1.16 [s, 3H, Me(AcO)]. ¹³C{¹H} NMR data [36]: δ = 182.5 [C(=O)O(AcO)], 153.1 (C^{3v}), 140.1 (d, ²J_{P–C} = 10.1 C^{2v}), 138.6 (C^{1v}), 135.4 (C^{5v}), 131.8 (C^{6v}), 135.0, 131.3, 129.2 and 128.4 (d, aromatic ¹³C nuclei of the PPh₃ ligand), 124.6 (C^{5v}), 123.7 (C^{4v}), 120.1 (C^{4v}), 113.7 (C^{2v}), 88.0 (C¹), 69.2 (C₅H₅), 68.1 (C² and C⁵), 67.7 (C³ and C⁴), 23.9 (–CH₂–), 23.0 [Me(AcO)], 13.8 (Me^b) and 13.7 (Me^a). ³¹P{¹H} NMR data: 44.3.

3.2.7. [Pd{κ²-C,N-C₆H₃-4-R-1-[(3,5-Me₂-C₃N₂)-CH₂-(η⁵-C₅H₄)Fe(η⁵-C₅H₅)]Cl(PPh₃)] (**6**) [R = OMe (**6a**) or H (**6b**)]

These products can be obtained by two different procedures using either the corresponding complex **3** or the monomeric derivative **4** [methods (a) and (b), respectively].

Method (a): To a solution containing a 50 mg (4.61 × 10^{−5} mol) of **3a** [or 30 mg (2.93 × 10^{−5} mol) of **3b**] and 50 mL of CH₂Cl₂, triphenylphosphine [24 mg (9.16 × 10^{−5} mol) for **6a** or 15 mg (5.72 × 10^{−5} mol) for **6b**] was added. The resulting mixture was stirred at 298 K for 1 h and filtered. The filtrate was concentrated to dryness on a rotary evaporator and the solid formed was passed through a short SiO₂ column (1.0 cm × 2.0 cm). Elution with a mixture of CH₂Cl₂:MeOH (100:0.2) produced the release of a yellow band which was collected and concentrated to dryness on a rotary evaporator. The solid formed was dried in vacuum for one day [yields: 52 mg (70%) and 33 mg (72%) for **6a** and **6b**, respectively].

Method (b): A 50 mg amount (6.2 × 10^{−5} mol of **5a** or 6.5 × 10^{−5} mol of **5b**) the corresponding complex [Pd{κ²-C,N-C₆H₃-4-R-1-[(3,5-Me₂-C₃N₂)-CH₂-(η⁵-C₅H₄)Fe(η⁵-C₅H₅)](AcO)(PPh₃)] (**5**) [R = OMe (**5a**) or H (**5b**)] was dissolved in 10 mL of acetone. Then, 10 mg (9.5 × 10^{−5} mol) of LiCl was added. The reaction mixture was stirred at 298 K for 2 h and then filtered out. The resulting yellow filtrate was concentrated to ca. 2 mL on a rotary evaporator.

Addition of *n*-hexane followed by slow evaporation of the solvents at 4 °C produced the precipitation of the complexes. The solids were collected by filtration and then dried in vacuum for one day [yields: 34 mg (70%) and 31 mg (67%) for **6a** and **6b**, respectively]. *Characterization data for 6a*: Anal. Calc. for $C_{41}H_{38}ClN_2FeOPPd$: C, 61.29; H, 4.77; N, 3.49. Found: C, 61.06; H, 4.68; N, 3.27%. MS (ESI⁺): 767 {[M]–Cl}⁺. IR-data: 3060(m), 3048(m), 2958(m), 2917(m), 1576(s), 1474(s), 1429(m), 122(s), 1095(s), 1038(s), 692(s), 530(m), 510(m) and 493(m) cm⁻¹. ¹H NMR data [36]: δ = 7.30–7.68 (m, 15H, aromatic protons of the PPh₃ ligand), 7.04 (dd, 1H, *J* = 7.5 and 2, H^{6''}), 6.38 (dd, 1H, *J* = 7.5 and 2, H^{5''}), 6.16 (d, 1H, *J* = 7.5, H^{3''}), 4.12 (s, 5H, C₅H₅), 4.09 (s, 2H, H² and H⁵), 4.04 (s, 2H, H³ and H⁴), 3.45 (s, 2H, –CH₂–), 2.94 (s, 3H, OMe), 2.69 (s, 3H, 2Me^a) and 2.42 (s, 3H, 2Me^b). ¹³C{¹H} NMR data [36]: δ = 154.9 (C^{3''}), 153.8 (C^{3'}), 147.3 (d, *J*_{P–C} = 9.6, C^{2''}), 136.1 (C^{5'}), 135.3 (C^{1''}), 135.1, 131.2, 129.0 and 128.2 (d, aromatic ¹³C nuclei of the PPh₃ ligand), 125.9 (C^{6''}), 120.2 (C^{5''}), 114.8 (C^{4'}), 111.2 (C^{4''}), 88.0 (C¹), 68.9 (C₅H₅), 68.5 (C² and C⁵), 67.6 (C³ and C⁴), 55.0 (OMe) 23.8 (–CH₂–), 13.4 (Me^a) and 13.0 (Me^b). ³¹P{¹H} NMR data: δ = 45.82. *For 6b*: Anal. Calc. for $C_{40}H_{36}ClN_2FePPd$: C, 62.10; H, 4.69; N, 3.62. Found: C, 62.35; H, 4.80; N, 3.73%. MS (ESI⁺): 737 {[M]–Cl}⁺. IR-data: 3090(w), 3053(w), 2904(w), 1476(s), 1433(s), 1383(m), 1097(s), 1020(m), 997(m), 744(s), 701(s), 688(s), 560(s), 514(s), 496(s) and 483(m) cm⁻¹. ¹H NMR data [36]: δ = 7.30–7.72 (m, 15H, aromatic protons of the PPh₃ ligand), 7.14 (dd, 1H, *J* = 7.5 and 2, H^{6''}), 6.85 (td, 1H, *J* = 7.5 and 2, H^{5''}), 6.57 (d, *J* = 7.5, H^{3''}), 6.29 (td, 2H, *J* = 7.5 and 2, H^{4''}), 4.13 (s, 5H, C₅H₅), 4.10 (s, 2H, H² and H⁵), 4.04 (s, 2H, H³ and H⁴), 3.51 (s, 2H, –CH₂–), 2.73 (s, 3H, 2Me^a) and 2.51 (s, 3H, 2Me^b). ¹³C{¹H} NMR data [36]: δ = 155.1 (C^{3''}), 152.4 (C^{3'}), 146.1 (C^{2''}), 140.3 (C^{1''}), 135.8 (C^{5'}), 135.1, 131.2, 129.3 and 128.2 (d, aromatic ¹³C nuclei of the PPh₃ ligand), 130.7 (C^{6''}), 124.3 (C^{5''}), 123.8 (C^{4''}), 114.4 (C^{4'}), 87.2 (C¹), 69.6 (C₅H₅), 68.6 (C² and C⁵), 67.6 (C³ and C⁴), 23.9 (–CH₂–), 13.5 (Me^b), and 13.3 (Me^a). ³¹P{¹H} NMR data: δ = 45.70.

3.2.8. [Pd{κ²-C,N-C₆H₃-4-R-1-[(3,5-Me₂-C₃N₂)-CH₂-(η⁵-C₅H₄)Fe(η⁵-C₅H₅)](acac)] (7) [R = OMe (7a) or H (7b)]

A mixture formed by the corresponding complex **3** [80 mg (7.4 × 10⁻⁵ mol) of **3a** or 75 mg (7.3 × 10⁻⁵ mol) of **3b**] and 40 mL of acetone was treated carefully with thallium(I) acetylacetonate [45 mg (14.8 × 10⁻⁵ mol) for **7a** or 44 mg (14.5 × 10⁻⁵ mol) for **7b**]. The resulting mixtures were stirred overnight at 298 K. The precipitate formed (TlCl) was removed by filtration with Whatman paper and the filtrate was concentrated to dryness on a rotary evaporator. The residue formed was treated with ca. 5 mL of CH₂Cl₂ and the undissolved material were removed by filtration with Whatman paper. Concentration of the filtrate to dryness on a rotary evaporator produced compounds **7** as yellow solids [yields: 60 mg (67%) for **7a** and 58 mg (69%) for **7b**]. *Characterization data for 7a*: Anal. Calc. for $C_{28}H_{30}N_2O_3FePd$: C, 55.60; H, 5.00; N, 4.63. Found: C, 55.32; H, 5.18; N, 4.50%. MS (ESI⁺): *m/z* = 604.1 [M⁺]. IR data: 3092(m), 3068(m), 2942(m), 2828(m), 1571(s), 1518(s), 1396(s), 1270(s), 1225(s), 1050(m), 1018(m), 782(m), 473(m) and 489(m) cm⁻¹. ¹H NMR data [36]: δ = 7.16 (td, *J* = 7.5 and 2.0, H^{6''}),

7.06 (dd, *J* = 7.5 and 2.0, H^{5''}), 6.60 (d, *J* = 2.0, H^{3''}), 5.38 [s, 1H, >CH(acac)], 4.13 (s, 5H, C₅H₅), 4.06 (t, 2H, *J* = 1.5, H² and H⁵), 4.03 (t, 2H, *J* = 1.5, H³ and H⁴), 3.51 (s, 3H, OMe), 3.48 (s, 2H, –CH₂–), 2.55(s, 3H, Me^a), 2.52 (s, 3H, Me^b), 2.07 (s, 3H, Me^c) and 1.99 (s, 3H, Me^d). ¹³C{¹H} NMR data [36]: δ = 188.5 and 188.9 [>CO(acac)], 151.1 (C^{3'}), 150.2 (C^{4''}), 145.3 (C^{2''}), 136.4 (C^{1''}), 135.6 (C^{5'}), 128.6 (C^{6''}), 119.0 (C^{4'}), 116.3 (C^{5''}), 111.6 (C^{3''}), 100.2 [>CH(acac)], 87.7 (C^{1'}), 69.9 (C₅H₅), 68.4 (C^{2'} and C^{5'}), 67.7 (C³ and C⁴), 55.6 (OMe), 27.8 (Me^c and Me^d), 23.5 (–CH₂–), 12.4 (Me^b) and 10.6 (Me^a). *For 7b*: Anal. Calc. for $C_{27}H_{28}N_2O_2FePd$: C, 56.42; H, 4.91; N, 4.87. Found: C, 56.31; H, 5.05; N, 4.62%. MS (ESI⁺): *m/z* = 574.1 [M⁺]. IR: 3067(m), 2956(m), 2922(m), 1587(s), 1513(s), 1463(m), 1443(m), 1399(m), 1019(m), 1034(m), 503(m) and 485(m) cm⁻¹. ¹H NMR data [36]: 7.57 (td, 1H, ³*J* = 7.5 and 2.0, H^{6''}), 7.06 (td, *J* = 7.5, 2.0, H^{5''}), 7.13 (dd, *J* = 7.5, 2.0, H^{3''}), 6.97 (td, *J* = 7.5, 2.0, H^{4''}), 5.36 [s, 1H, >CH(acac)], 4.14 (s, 5H, C₅H₅), 4.02 (t, 2H, ³*J* = 1.5, H² and H⁵), 3.97 (t, 2H, ³*J* = 1.5, H³ and H⁴), 3.57 (s, 2H, –CH₂–), 2.57 (s, 3H, Me^a), 2.53 (s, 3H, Me^b), 2.06 (s, 3H, Me^c) and 1.98 (s, 3H, Me^d). ¹³C{¹H} NMR data [36]: 188.0 and 188.3 [>CO(acac)], 151.1 (C^{3'}), 145.3 (C^{2''}), 136.3 (C^{1''}), 135.1 (C^{5'}), 131.8 (C^{6''}), 124.8 (C^{5''}), 123.7 (C^{4''}), 119.5 (C^{4'}), 112.9 (C^{3''}), 100.1 [>CH(acac)], 87.8 (C^{1'}), 69.8 (C₅H₅), 68.4 (C^{2'} and C^{5'}), 67.7 (C³ and C⁴), 23.7 (–CH₂–), 27.1 (Me^c and Me^d), 10.5 (Me^a) and 12.4 (Me^b).

3.2.9. [Pd{(MeO₂C–C≡C–CO₂Me)₂(C₆H₃-4-R-1-[(3,5-Me₂-C₃N₂)-CH₂-(η⁵-C₅H₄)Fe(η⁵-C₅H₅)]Cl)] (8) [R = OMe (8a) or H (8b)]

A 8.1 × 10⁻⁴ mol amount of the corresponding di-μ-chloro-bridged complex **3** [83 mg of **3a** or 88 mg of **3b**] was suspended in 30 mL of CH₂Cl₂. Then MeO₂C–C≡C–CO₂Me [0.4 mL (32.5 × 10⁻⁴ mol)] was added dropwise under vigorous stirring at 298 K. Once the addition had finished the reaction mixture was refluxed for one day and then concentrated on a rotary evaporator to ca. 5 mL. The deep-orange solution was passed through a short SiO₂ column (1.0 cm × 2.0 cm). Elution with a CH₂Cl₂:MeOH (100:0.1) mixture produced the release of a bright orange band that was collected and concentrated to dryness on a rotary evaporator. The residue was then dried under reduced pressure for one day [yields: 87 mg (67%) and 91 mg (68%) for **8a** and **8b**, respectively]. *Characterization data for 8a*: Anal. Calc. for $C_{35}H_{35}N_2O_9FePdCl$: C, 59.93; H, 4.27; N, 3.39. Found: C, 60.0; H, 4.30; N, 3.30%. MS (ESI⁺): *m/z* = 789.1 {[M]–Cl}⁺. IR data: 3084(m), 2997(m), 2947(m), 1731(broad, s), 1436(s), 1390(m), 1258(s), 1227(s), 1104(m), 1051(m), 1000(s), 819(m), 801(s) 499(m) and 481(m) cm⁻¹. *λ* (10⁻³ M in acetone at 298 K) = 12 Ω⁻¹ cm². ¹H NMR data [36]: δ = 7.12 (d, 1H, H^{6''}), 6.62 (d, 1H, H^{6''}), 6.50 (d, 1H, *J* = 7.5 and 2.0, H^{3''}), 4.10 (s, 5H, C₅H₅), 4.03 (t, 2H, *J* = 1.5, H² and H⁵), 3.98 (t, 2H, *J* = 1.5, H³ and H⁴), 3.77 (s, 3H, OMe), 3.71 (s, 3H, OMe), 3.69 (s, 3H, OMe), 3.52 (s, 2H, –CH₂–), 3.04 (s, 3H, OMe), 2.38 (s, 3H, Me^a) and 2.24 (s, 3H, Me^b). ¹³C{¹H} NMR data [36]: δ = 170.0, 165.9, 163.4 and 162.0 (4 >CO₂), 158.8 (C⁷), 154.6 (C^{4''}), 151.6 (C^{3'}), 151.4 (C^{2''}), 140.1 (C^{5'}), 139.4 (C⁶), 139.2 (C^{1''}), 137.2 (C^{6'}), 127.4 (C^{6''}), 122.3 (C^{2'}) 116.7 (C^{5''}), 112.9 (C^{4'}), 111.7 (C^{3''}), 86.7 (C^{1'}), 69.8 (C₅H₅), 68.4 (C^{2'} and C^{5'}), 67.5 (C³ and C⁴), 58.7, 53.8, 53.2 and 53.0 (4 OMe), 24.5 (–CH₂–), 12.6 (Me^b) and 11.7 (Me^a). *For 8b*: Anal. Calc. for $C_{34}H_{33}N_2O_8FePdCl$: C, 51.34; H, 4.18; N, 3.52. Found: C, 51.27; H, 4.22; N, 3.50%. (ESI⁺): *m/z* = 759.0 {[M]–Cl}⁺. IR: 3088(m), 2991(m), 2950(m), 1724(s), 1432(s), 1376(m), 1260(s), 1226(s), 1103(m), 1021(m), 801(s) and 481(m) cm⁻¹. *λ* (10⁻³ M in acetone at 298 K) = 18 Ω⁻¹ cm². ¹H NMR data [36]: δ = 7.21 (dd, 1H, *J* = 7.5 and 2.0, H^{6''}), 7.02–7.15 (m, 2H, H^{4''} and H^{5''}), 6.53 (d, 1H, *J* = 7.5 and 2.0, H^{3''}), 4.08 (s, 5H, C₅H₅), 4.02 (t, 2H, *J* = 1.5, H² and H⁵), 3.97 (t, 2H, *J* = 1.5, H³ and H⁴), 3.78 (s, 3H, OMe), 3.74 (s, 3H, OMe), 3.72 (s, 3H, OMe), 3.50 (s, 2H, –CH₂–), 3.05 (s, 3H, OMe), 2.40 (s, 3H, Me^a) and 2.26 (s, 3H, Me^b). ¹³C{¹H} NMR data [36]: 169.9, 165.8, 163.2

and 161.1 ($4 > \text{CO}_2$), 157.9 (C^1), 151.9 ($\text{C}^{3''}$), 151.4 ($\text{C}^{3'}$), 142.5 ($\text{C}^{2''}$), 139.9 ($\text{C}^{5'}$), 139.2 ($\text{C}^{1''}$), 138.2 (C^6), 137.0 (C^6), 128.5 ($\text{C}^{6''}$), 123.9 ($\text{C}^{5''}$), 123.0 ($\text{C}^{4''}$), 119.1 (C^3), 112.0 ($\text{C}^{4''}$), 86.8 ($\text{C}^{1'}$), 69.8 (C_5H_5), 68.5 ($\text{C}^{2'}$ and $\text{C}^{5'}$), 67.5 (C^3 and C^4), 58.8, 52.8, 53.1 and 53.8 (4 OMe), 24.6 ($-\text{CH}_2-$), 12.6 (Me^b) and 12.1 (Me^a).

3.3. Electrochemical studies

Electrochemical data were obtained by cyclic voltammetry under nitrogen at 298 K using acetonitrile (HPLC grade) as solvent, tetrabutylammonium hexafluorophosphate $\{(\text{Bu}_4\text{N})[\text{PF}_6], 0.1 \text{ M}\}$ as supporting electrolyte and a potentiostat M263A from EG&G instruments. The potentials were referred to an Ag–AgNO₃ (0.1 M in acetonitrile) electrode separated from the solution by a medium porosity fritted disk. A platinum wire auxiliary electrode was used in conjunction with a platinum disc working Tacussel-Edi rotatory electrode (3.14 mm²). Cyclic voltammograms of ferrocene were recorded before and after each sample to ensure the stability of the Ag–AgNO₃ electrode. Cyclic voltammograms of freshly prepared solutions (10^{-3} M) of the samples in acetonitrile were run and the average values of the potentials were then referred to ferrocene, which was used as internal reference. Under these experimental conditions the standard error of the measured potentials was $\pm 5 \text{ mV}$. In all the experiments, cyclic voltammograms were registered using scan speeds (v) varying from 10 mV/s^{-1} to 100 mV/s^{-1} .

3.4. Crystallography

A prismatic crystal of **6b** · CH₂Cl₂ (sizes in Table 2) was selected and mounted on a Enraf-Nonius CAD4 four-circle diffractometer. Unit-cell parameters were determined from automatic centering of 25 reflections ($12^\circ < \theta < 21^\circ$) and refined by least-squares method. Intensities were collected with graphite monochromatized Mo K α radiation, using $\omega/2\theta$ scan-technique. The number of reflections measured in the range $2.14^\circ \leq \theta \leq 29.97^\circ$ was 12292 reflections of

which 5092 were assumed as observed applying the condition $I > 2\sigma(I)$. Three reflections were measured every 2 h as orientation and intensity control, significant intensity decay was not observed. Lorentz-polarization and absorption corrections were made.

The structure was solved by Direct methods, using SHELXS computer program [37] and refined by full-matrix least-squares method with SHELXL97 computer program [38] using 17813 reflections, (very negative intensities were not assumed). The function minimized was $\sum w||F_o|^2 - |F_c|^2|^2$, where $w = [\sigma^2(I) + (0.0657P)^2]^{-1}$, and $P = (|F_o|^2 + 2|F_c|^2)/3$; f , f' and f'' were taken from the bibliography [39]. The molecule of CH₂Cl₂ was disordered and the positions of its atoms were fixed. The remaining hydrogen atoms were computed and refined, using a riding model, with an isotropic temperature factor equal to 1.2 time the equivalent temperature factor of the atom which are linked. The final R (on F) factor was 0.043, wR (on $|F|^2$) = 0.141 and goodness of fit = 0.889 for all observed reflections. Number of refined parameters was 449. Max. shift/esd = 0.00, Mean shift/esd = 0.00. Max. and min. peaks in final difference synthesis was 0.783 and $-0.608 \text{ e } \text{Å}^{-3}$, respectively. Further details concerning the solution and refinement of this crystal structure are presented in Table 2.

Acknowledgements

Financial support from the Ministry of Science and Technology (CTQ2006-0207 and CTQ2006-02390/BQU) is gratefully acknowledged.

Appendix A. Supplementary material

CCDC 673141 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2008.02.033](https://doi.org/10.1016/j.jorganchem.2008.02.033).

References

- (a) For a general overview on cyclopalladated compounds and their applications, see: I. Omae, Applications of Organometallic Compounds, Wiley, Chichester, UK, 1998 [Chapter 20, p. 423]; (b) A.J. Klaus, in: A.E. Peters, H.S. Freeman (Eds.), Modern Colorants, Synthesis and Structure, vol. 3, Blackie Academic, London, UK, 1995, p. 1; (c) N.J. Thompson, J.L. Serrano, M.J. Baena, P. Espinet, Chem. Eur. J. 2 (1996) 214; (d) S.B. Wild, Coord. Chem. Rev. 166 (1997) 291; (e) J. Spencer, M. Pfeffer, Adv. Met. Org. Chem. 6 (1998) 103; (f) M. Pfeffer, Recl. Trav. Chim. Pays-Bas 109 (1990) 567; (g) A.D. Ryabov, Synthesis (1985) 233. and references cited therein.
- (a) For applications of palladacycles in homogeneous catalysis, see: A.S. Gruber, D. Zim, G. Ebeling, A.L. Monteiro, Org. Lett. 2 (2000) 2187; (b) J. Dupont, M. Pfeffer, J. Spencer, Eur. J. Inorg. Chem. (2001) 1917; (c) X. Gai, R. Grigg, M.I. Ramzan, V. Sridharan, S. Collard, J.E. Muir, Chem. Commun. (2000) 2053. and references cited therein.
- (a) For examples of the antitumoral activity of cyclopalladated complexes: J.D. Higgins, L. Neely, S.J. Fricker, J. Inorg. Biochem. 49 (1993) 149; (b) C. Navarro-Ranninger, I. López-Solera, J.M. Pérez, J.R. Masaguer, C. Alonso, Appl. Organomet. Chem. 7 (1993) 57; (c) C. Navarro-Ranninger, I. López-Solera, V.M. González, J.M. Pérez, A. Alvarez-Valdes, A. Martín, P.R. Raithby, J.R. Masaguer, C. Alonso, Inorg. Chem. 35 (1996) 5181.
- (a) For macromolecules containing cyclopalladated units, see: M. López-Torres, A. Fernández, J.J. Fernández, A. Suárez, S. Castro-Juiz, J.M. Vila, M.T. Pereira, Organometallics 20 (2001) 1350; (b) C. López, A. Caubet, S. Pérez, X. Solans, M. Font-Bardía, J. Organomet. Chem. 681 (2003) 80; (c) A. Fernández, E. Pereira, J.J. Fernández, M. López-Torres, A. Suarez, R. Mosteiro, M.T. Pereira, J.M. Vila, New J. Chem. 26 (2002) 895.
- (a) For recent examples of the use of palladacycles in organic and organometallic synthesis, see: D. Solé, L. Vallverdú, X. Solans, M. Font-Bardía, J. Bonjoch, Organometallics 24 (2004) 1438; (b) D. Solé, L. Vallverdú, X. Solans, M. Font-Bardía, J. Bonjoch, J. Am. Chem. Soc. 125 (2003) 1587;

Table 2

Crystal data and details of the refinement of the crystal structure of compound **6b** · CH₂Cl₂

Crystal size (mm × mm × mm)	0.1 × 0.1 × 0.2
Empirical formula	C ₄₁ H ₃₈ Cl ₃ FeN ₂ PPd
Molecular weight	858.30
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	15.506(4)
<i>b</i> (Å)	10.206(14)
<i>c</i> (Å)	27.155(11)
α (°)	90
β (°)	104.37(3)
γ (°)	90
Temperature (K)	293(2)
λ (Å)	0.71073
<i>V</i> (Å ³)	4163(6)
<i>Z</i>	4
<i>D</i> _{calc} (mg × m ⁻³)	1.369
μ (mm ⁻¹)	1.040
<i>F</i> (000)	1744
Θ -range for data collection (°)	2.14–29.96
No. or collected reflections	12292
No. of unique reflections	12071 [<i>R</i> (int) = 0.0502]
Completeness to Θ	99.8%
No. of data	12071
No. of parameters	449
Refinement method	SHELXL-97
Goodness of fit on <i>F</i> ²	0.889
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0434, <i>wR</i> ₂ = 0.1084
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1540, <i>wR</i> ₂ = 0.1415
Largest diffraction peak and hole	0.783 and -0.608

- (c) N. Gul, J.H. Nelson, A.C. Willis, A.D. Ross, *Organometallics* 21 (2002) 2041;
(d) S. Pérez, C. López, A. Caubet, A. Pawelczyk, X. Solans, M. Font-Bardía, *Organometallics* 22 (2003) 2396.
- [6] (a) For advances in the cyclopalladation process, see: I. Omae, *J. Organomet. Chem.* 692 (2007) 2608;
(b) K. Godula, D. Sames, *Science* 312 (2006) 67;
(c) J. Dupont, C.S. Consorti, J. Spencer, *Chem. Rev.* 105 (2005) 2527;
(d) C. López, S. Pérez, X. Solans, M. Font-Bardía, A. Roig, E. Molins, P.W.N.M. van Leeuwen, G.P.F. van Strijdonck, *Organometallics* 26 (2007) 571;
(e) T.-K. Zhang, K. Yuan, X.-L. Hou, *J. Organomet. Chem.* 692 (2007) 1912;
(f) P.G. Evans, N.A. Brown, G.J. Clarkson, C.P. Newman, J.P. Rourke, *J. Organomet. Chem.* 691 (2006) 1251;
(g) S. Pérez, C. López, A. Caubet, X. Solans, M. Font-Bardía, A. Roig, E. Molins, *Organometallics* 25 (2006) 596;
(h) A. Moyano, M. Rosol, R.M. Moreno, C. López, M.A. Maestro, *Angew. Chem., Int. Ed.* 44 (2005) 1865;
(i) M.E. Weiss, D.F. Fischer, Z. Xin, S. Jautze, W.B. Schweizer, R. Peters, *Angew. Chem., Int. Ed.* 45 (2006) 5694;
(j) C.E. Anderson, Y. Donde, D. Yariv, J. Christopher, L.E. Overman, *J. Org. Chem.* 70 (2005) 648.
- [7] A. Togni, T. Hayashi (Eds.), *Ferrocenes. Homogeneous Catalysis, Organic Synthesis*. Materials Science, VCH, Weinheim (Germany), 1995.
- [8] (a) R. Gómez Arrayas, J. Adrio, J.C. Carretero, *Angew. Chem., Int. Ed.* 45 (2006) 7674;
(b) D.R. van Staveren, N. Metzler-Nolte, *Chem. Rev.* 104 (2004) 5931.
- [9] (a) T.K. Hollis, L.E. Overman, *J. Organomet. Chem.* 576 (1999) 290;
(b) Y. Donde, L.E. Overman, *J. Am. Chem. Soc.* 121 (1999) 2933.
- [10] A. Gonzalez, J. Granell, C. López, *J. Organomet. Chem.* 637–639 (2001) 116.
- [11] M.T. Alonso, O. Juanes, J. de Mendoza, J.C. Rodríguez-Ubis, *J. Organomet. Chem.* 430 (1992) 335.
- [12] (a) V.I. Boev, L.V. Snegur, V.N. Babin, Y.S. Nekresov, *Russ. Chem. Rev.* 66 (1997) 613;
(b) K. Pagel, A. Werner, W. Friedrichsen, *J. Organomet. Chem.* 481 (1994) 109.
- [13] A. González, J. Marquet, M. Moreno-Mañas, *Tetrahedron* 42 (1986) 4253.
- [14] *Gmelin Handbuch der Anorganische Chemie. Eisen Organische Verbindungen. Ferrocen*. Springer-Verlag, Heidelberg, (Germany) 1977–1986, part A1–A8.
- [15] C. López, R. Bosque, X. Solans, M. Font-Bardía, *New J. Chem.* 20 (1996) 1285.
- [16] W.E. Geiger, *Organometallics* 26 (2007) 5738.
- [17] E.R. Brown, J.R. Sandifer, in: B.W. Rossiter, J.H. Hamilton (Eds.), *Physical Methods in Chemistry: Electrochemical Methods*, vol. 4, Wiley, New York, USA, 1986 (Chapter 4).
- [18] (a) N.F. Blom, E.W. Neuse, H.G. Thomas, *Trans. Met. Chem.* 12 (1987) 301;
(b) P. Zanello, A. Cinquantini, S. Mangani, G. Opromolla, L. Pardi, C. Janiak, M.D. Rausch, *J. Organomet. Chem.* 471 (1994) 171;
(c) G.L.K. Hoh, W.E. McEwen, J. Kleinberg, *J. Am. Chem. Soc.* 83 (1961) 3949.
- [19] (a) R. Bosque, C. López, J. Sales, *Inorg. Chim. Acta* 244 (1995) 141;
(b) X. Riera, A. Caubet, C. López, V. Moreno, *Inorg. Chim. Acta* 18 (1999) 2549.
- [20] (a) T. Mochida, F. Shimizu, H. Shimizu, K. Okazawa, F. Sato, D. Kuwahara, *J. Organomet. Chem.* 692 (2007) 1834;
(b) T. Mochida, H. Shimizu, S. Suzuki, T. Akasaka, *J. Organomet. Chem.* 691 (2006) 4882;
(c) M. Zora, A.N. Pinar, M. Odabasoglu, O. Büyükgüngör, G. Turgut, *J. Organomet. Chem.* 693 (2008) 145.
- [21] K. Nakamoto, *IR and Raman Spectra of Inorganic and Coordination Compounds*, 5th ed., Wiley, New York, USA, 1997.
- [22] F.H. Allen, *Acta Crystallogr., Sect. B* 58 (2002) 380.
- [23] (a) C. Navarro-Ranninger, F. Zamora, I. López-Solera, A. Monge, J.R. Masaguer, *J. Organomet. Chem.* 506 (1996) 149;
(b) J. Albert, L. D'Andrea, J. Granell, R. Tavera, M. Font-Bardía, X. Solans, *J. Organomet. Chem.* 692 (2007) 3070.
- [24] (a) A. Fernández, D. Vázquez-García, J.J. Fernández, M. Lopez-Torres, A. Suarez, J.M. Vila, *J. Organomet. Chem.* 690 (2005) 3669;
(b) X. Riera, C. López, A. Caubet, V. Moreno, X. Solans, *Eur. J. Inorg. Chem.* (2001) 2135;
(c) X. Riera, A. Caubet, C. López, V. Moreno, E. Freisinger, M. Willermann, B. Lippert, *J. Organomet. Chem.* 629 (2001) 97.
- [25] (a) R. Bosque, C. López, J. Sales, X. Solans, *Dalton Trans.* (1994) 735;
(b) A. Fernández, D. Vázquez-García, J.J. Fernández, M. López-Torres, A. Suárez, S. Castro-Juiz, J.M. Vila, *New J. Chem.* 26 (2002) 398.
- [26] C. Hansch, A. Leo, D. Koekman, *Exploring QSAR. Hydrophobic, Electronic and Steric Constants*, American Chemical Society, Washington, DC, USA, 1995.
- [27] (a) J. Vicente, A. Arcas, D. Bautista, P.G. Jones, *Organometallics* 16 (1997) 2127;
(b) J. Vicente, J.A. Abad, A.D. Frankland, M.C. Ramirez De Arellano, *Chem. Eur. J.* 5 (1999) 3066;
(c) J. Vicente, J.A. Abad, E. Martínez-Viviente, P.G. Jones, *Organometallics* 21 (2002) 4454.
- [28] (a) A. Bondi, *J. Phys. Chem.* 64 (1964) 441;
(b) A.I. Kitaigorodskii, *Molecular Crystals and Molecules*, Academic Press, London, UK, 1973;
(c) T. Steiner, *Acta Crystallogr., Sect. B* 54 (1998) 456.
- [29] G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), *Comprehensive Organometallic Chemistry. The Synthesis, Reactions and Structure of Organometallic Compounds*, vol. 6, Pergamon Press, New York, USA, 1982, p. 236.
- [30] Attempts to prepare a 10^{-3} M molar solutions of 2 in acetonitrile (HPLC-grade) showed that the initial powdered solid sample of 2 did not dissolved completely and the initial solid sample turn into a gummy material. Complete dissolution or destruction of this residue was not achieved after stirring the mixture for 24 h at 298 K.
- [31] (a) C. López, J. Granell, *J. Organomet. Chem.* 555 (1998) 211;
(b) W.F. Little, C.N. Reilly, J.D. Johnson, A.P. Saunders, *J. Am. Chem. Soc.* 86 (1964) 1376;
(c) A. Benito, J. Cano, R. Martínez-Mañez, J. Soto, M.J.L. Tendero, J. Payá, E. Sinn, *Inorg. Chim. Acta* 210 (1993) 233;
(d) A. Louati, M. Gross, L. Duce, D. Matt, *J. Organomet. Chem.* 438 (1992) 167;
(e) M. Bracci, E. Ercolani, B. Floris, M. Bassetti, A. Chiesi-Villa, C. Guastini, *Dalton Trans.* (1990) 1357.
- [32] (a) C. López, R. Bosque, X. Solans, M. Font-Bardía, J. Silver, G. Fern, *Dalton Trans.* (1995) 1839;
(b) M. Benito, C. López, X. Morvan, X. Solans, M. Font-Bardía, *Dalton Trans.* (2000) 4470;
(c) C. López, S. Pérez, X. Solans, M. Font-Bardía, *J. Organomet. Chem.* 690 (2005) 228.
- [33] W.J. Geary, *Coord. Chem. Rev.* 7 (1971) 87.
- [34] (a) W. Tao, L.J. Silverberg, A.L. Rheingold, R.F. Heck, *Organometallics* 8 (1989) 2550;
(b) J.P. Sutter, M. Pfeffer, A. de Cian, J. Fischer, *Organometallics* 11 (1992) 386;
(c) M. Pfeffer, J.P. Sutter, A. De Cian, J. Fischer, *Inorg. Chim. Acta* 220 (1994) 115;
(d) A. Albinati, P.S. Pregosin, R. Ruedi, *Helv. Chim. Acta* 67 (1985) 2029;
(e) G. Zhao, Q.G. Wang, T.C.W. Mak, *J. Organomet. Chem.* 574 (1999) 311;
(f) G. Zhao, Q.G. Wang, T.C.W. Mak, *Tetrahedron: Asymm.* (1998) 2253;
(g) G. Zhao, Q.G. Wang, T.C.W. Mak, *Tetrahedron: Asymm.* (1998) 1557.
- [35] D.D. Perrin, W.L.F. Amarego, D.L. Perrin, *Purification of Laboratory Chemicals*, 3rd ed., Butterworth-Heinemann, Oxford, UK, 1988.
- [36] For the free ligands labeling of the atoms refers to those shown in Schemes 1 and 2; while for the palladium(II) complexes the numbering sequence is presented in Scheme 2 (for 2–6) and 3 (for 7 and 8).
- [37] G.M. Sheldrick, *SHELXS* A program for automatic solution of crystal structure, University of Goettingen, Germany, 1997.
- [38] G.M. Sheldrick, *SHELX97* A program for automatic solution of crystal structure, University Goettingen, Germany, 1997.
- [39] *International Tables of X-Ray Crystallography*, Ed. Kynoch Press, 1974 vol. IV, pp. 99–100 and 149, Birmingham, UK.