

# Alkyne Insertions into the $\sigma$ -Pd–C(sp<sup>2</sup>, ferrocene) Bond of Cyclopalladated Complexes containing Schiff Bases derived from Ferrocene. Crystal Structures of [Pd{[(EtC=CET)<sub>2</sub>( $\eta^5$ -C<sub>5</sub>H<sub>3</sub>CR=N-CH<sub>2</sub>Ph)]Fe( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)}Cl] (R = H or Me)†

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Reactions of di- $\mu$ -chloro-bridged cyclopalladated compounds [ $\{\text{Pd}[(\eta^5\text{-C}_5\text{H}_3\text{CR}=\text{NR}')\text{Fe}(\eta^5\text{-C}_5\text{H}_5)](\mu\text{-Cl})\}_2$ ] (R = H, Ph or Me, R' = CH<sub>2</sub>Ph; R = H, R' = CH<sub>2</sub>CH<sub>2</sub>Ph) with alkynes R''C $\equiv$ CR'' (R'' = Et or Ph) have been studied. In all cases these reactions produce nine-membered metallocycles [ $\text{Pd}\{[(\text{R}''\text{C}=\text{CR}'')_2(\eta^5\text{-C}_5\text{H}_3\text{CR}=\text{NR}')\text{Fe}(\eta^5\text{-C}_5\text{H}_5)]\text{Cl}\}$ ] (R'' = Et or Ph), which arise from a double insertion of the alkyne. Compounds [ $\text{Pd}\{[(\text{EtC}=\text{CEt})_2(\eta^5\text{-C}_5\text{H}_3\text{CR}=\text{NCH}_2\text{Ph})\text{Fe}(\eta^5\text{-C}_5\text{H}_5)]\text{Cl}\}$ ] (R = H **4a** or Me **4d**) have been characterized structurally. Complex **4a** is monoclinic, space group C2/c, with  $a = 30.783(4)$ ,  $b = 11.320(2)$ ,  $c = 20.181(3)$  Å and  $\beta = 127.23(3)^\circ$ ; compound **4d** is also monoclinic space group P2<sub>1</sub>/a, with  $a = 20.308(4)$ ,  $b = 11.075(2)$ ,  $c = 12.565(2)$  Å and  $\beta = 92.01(3)^\circ$ . These structural studies confirm the existence of a bicyclic system arising from the fusion of a nine-membered ring and the C<sub>5</sub>H<sub>3</sub> moiety of the ferrocenyl moiety. The differences observed in the reactivity of the  $\sigma(\text{Pd}-\text{C}_{\text{sp}^2, \text{ferrocene}})$  bond in the cyclopalladated compounds [ $\{\text{Pd}[(\eta^5\text{-C}_5\text{H}_3\text{CR}=\text{NR}')\text{Fe}(\eta^5\text{-C}_5\text{H}_5)](\mu\text{-Cl})\}_2$ ] (R = H, Ph or Me) and in [ $\{\text{Pd}[(\eta^5\text{-C}_5\text{H}_3\text{CH}_2\text{NMe}_2)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)](\mu\text{-Cl})\}_2$ ] can be explained in terms of the electron donor ability of the chelated ligand. This property is reflected mainly in the redox potential of the iron centre.

The study of *ortho*-palladated complexes containing N-donor ligands has increased considerably during the last decade<sup>1</sup> due to a variety of novel and interesting applications.<sup>2–6</sup> Potential applications of cyclopalladated derivatives include liquid crystals,<sup>2</sup> antitumour drugs,<sup>3</sup> and catalytic materials.<sup>4</sup> Furthermore, compounds of this kind have provided new methods for the synthesis of organic and organometallic compounds.<sup>6</sup> Most of these reactions are based on insertions of small molecules such as alkynes, alkenes or CO into the  $\sigma(\text{Pd}-\text{C})$  bond.<sup>6–9</sup>

Although it is well known that the reactivity of cyclopalladated complexes containing N-donor ligands with alkynes is dependent on several factors, including the electron donor/electron acceptor nature of the substituents on the alkyne, the cyclometallated ligand, the stoichiometry and even the remaining ligands co-ordinated to the palladium,<sup>6</sup> the relative importance of these factors has not been clearly established. Some attempts to clarify this point have recently been reported.<sup>6,7</sup> For instance, high-pressure kinetic studies on alkyne insertions into the  $\sigma(\text{Pd}-\text{C}_{\text{sp}^2, \text{phenyl}})$  bond in cyclopalladated derivatives containing *N,N*-dimethylbenzylamines [ $\{\text{Pd}(\text{C}_6\text{H}_3\text{RCH}_2\text{NMe}_2)(\mu\text{-X})\}_2$ ] (R = H, 4-OMe, 5-Me or 5-F; X = Cl or I) (Fig. 1, A) have revealed that: (a) the rate-determining step is the formation of the mono-insertion derivative, and (b) the presence of electron donor substituents R in the phenyl group enhances the rate constant, and consequently facilitates the insertion process.<sup>7</sup>

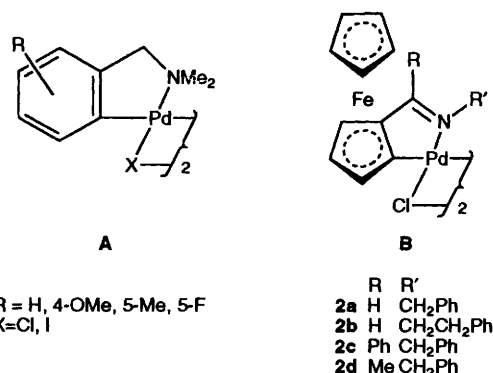


Fig. 1 Molecular scheme of five-membered cyclopalladated complexes derived from *N,N*-dimethylbenzylamine (A) and Schiff bases derived from ferrocene (B). These two types of derivative are characterized by the presence of a  $\sigma(\text{Pd}-\text{C}_{\text{sp}^2, \text{phenyl}})$  bond in A and a  $\sigma(\text{Pd}-\text{C}_{\text{sp}^2, \text{ferrocene}})$  bond in B

We have recently described<sup>10–12</sup> some novel five-membered palladocyclic complexes with  $\sigma(\text{Pd}-\text{C}_{\text{sp}^2, \text{ferrocene}})$  bonds derived from ferrocenyl Schiff bases of general formula [ $\{(\eta^5\text{-C}_5\text{H}_4)\text{CR}=\text{NR}'\}\text{Fe}(\eta^5\text{-C}_5\text{H}_5)]$  **1** (R = H, Me or Ph; R' = Ph, C<sub>6</sub>H<sub>4</sub>Me-2, C<sub>6</sub>H<sub>4</sub>Me-4, CH<sub>2</sub>Ph, CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Me-2, CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Cl-2 or CH<sub>2</sub>CH<sub>2</sub>Ph) and studied the influences of the R and R' substituents upon the spectroscopic and structural properties of not only the free ligands but also their di- and mono-nuclear cyclopalladated derivatives [ $\{\text{Pd}[(\eta^5\text{-C}_5\text{H}_3\text{CR}=\text{NR}')\text{Fe}(\eta^5\text{-C}_5\text{H}_5)](\mu\text{-Cl})\}_2$ ] **2** (Fig. 1, B)

† Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

and  $[\text{Pd}\{(\eta^5\text{-C}_5\text{H}_3\text{CR}=\text{NR}')\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}\text{Cl}(\text{L})]$  ( $\text{L}$  = neutral ligand) **3**, respectively.<sup>10-12</sup> In particular, electrochemical and Mössbauer spectroscopic studies have shown that the iron environment is highly sensitive to the changes introduced on the R and R' groups, as well as on the remaining ligands bound to the palladium.<sup>10a,11,12</sup> It has recently been reported that the cyclopalladated compound  $[\text{Pd}\{(\eta^5\text{-C}_5\text{H}_3\text{CH}=\text{NCH}_2\text{Ph})\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}(\mu\text{-Cl})_2]$  is clearly more reactive than derived organic imine analogues, such as  $[\text{Pd}(\text{C}_6\text{H}_4\text{CH}=\text{NR}')(\mu\text{-Cl})_2]$ , where the metallacycle contains a  $\sigma(\text{Pd}-\text{C}_{\text{sp}^2, \text{phenyl}})$  bond.<sup>13</sup> On the basis of these findings, complexes  $[\text{Pd}\{(\eta^5\text{-C}_5\text{H}_3\text{CR}=\text{NR}')\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}(\mu\text{-Cl})_2]$  **2** appear to be good substrates to study in order to clarify the effect of the chelated ligand (mainly reflected in the nature of the R substituent) upon the reactivity of the  $\sigma(\text{Pd}-\text{C}_{\text{sp}^2, \text{ferrocene}})$  bond with alkynes. In this paper we report a comparative study of the reactivity of  $[\text{Pd}\{(\eta^5\text{-C}_5\text{H}_3\text{CR}=\text{NR}')\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}(\mu\text{-Cl})_2]$  **2a-2d** ( $\text{R} = \text{H, Ph or Me, R}' = \text{CH}_2\text{Ph; R} = \text{H, R}' = \text{CH}_2\text{CH}_2\text{Ph}$ ) (Fig. 1, B) with alkynes, in particular, hex-3-yne and diphenylacetylene.

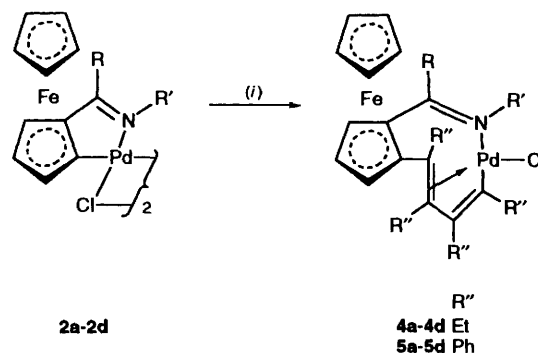
## Results and Discussion

**Syntheses and Characterization.**—Reactions of the di- $\mu$ -chloro-bridged cyclopalladated complexes  $[\text{Pd}\{(\eta^5\text{-C}_5\text{H}_3\text{CR}=\text{NR}')\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}(\mu\text{-Cl})_2]$  **2a-2d** ( $\text{R} = \text{H, Ph or Me, R}' = \text{CH}_2\text{Ph; R} = \text{H, R}' = \text{CH}_2\text{CH}_2\text{Ph}$ ) (Fig. 1, B) with alkynes  $\text{R}''\text{C}\equiv\text{CR}''$  ( $\text{R}'' = \text{Et or Ph}$ ), in a 1:4 molar ratio produce in all the cases studied  $[\text{Pd}\{[(\text{R}''\text{C}=\text{CR}'')_2(\eta^5\text{-C}_5\text{H}_3\text{CR}=\text{NR}')]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}\text{Cl}]$  compounds [ $\text{R}'' = \text{Et}$  (**4a-4d**) or  $\text{Ph}$  (**5a-5d**)] which arise from a bis(insertion) of the alkyne into the  $\sigma(\text{Pd}-\text{C}_{\text{sp}^2, \text{ferrocene}})$  bond (Scheme 1).

The new cyclopalladated complexes **4a-4d** and **5a-5d** are air-stable, orange-red solids. They are highly soluble in chloroform and dichloromethane, but only slightly soluble in alcohols and diethyl ether, and practically insoluble in *n*-hexane.

The infrared spectra of these compounds exhibit a sharp and intense band due to the asymmetric stretching of the C=N group that appears at lower wavenumbers than in the free ligands.<sup>10</sup> Similar observations on other five-membered cyclopalladated compounds derived from organic Schiff bases were attributed to a decrease in the C=N bond order. However, recent structural studies of the ligand  $[(\eta^5\text{-C}_5\text{H}_4\text{CPh}=\text{NPh})\text{Fe}(\eta^5\text{-C}_5\text{H}_5)]$  **1c** and the corresponding cyclopalladated derivative  $[\text{Pd}\{[(\eta^5\text{-C}_5\text{H}_3\text{CPh}=\text{NPh})]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}\text{Cl}(\text{PPh}_3)]$  **3c** have shown that the C=N bond is practically identical in the two compounds<sup>10c,11</sup> [1.308(9) and 1.308(8) Å respectively], and consequently the formation of the metallacycle does not significantly affect the C=N bond length.

Proton NMR data for the complexes  $[\text{Pd}\{[(\text{R}''\text{C}=\text{CR}'')_2(\eta^5\text{-C}_5\text{H}_3\text{CR}=\text{NR}')]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}\text{Cl}]$  are summarized in Table 1. The most relevant feature of the spectra is the existence of four singlets with relative intensities 5:1:1:1 in the range  $\delta$  3.7–4.6, which are ascribed to the protons of the C<sub>5</sub>H<sub>5</sub> moiety and to the three types of hydrogen nucleus on the 1,2-disubstituted ring of the ferrocenyl group, respectively. In complexes with  $\text{R}' = \text{CH}_2\text{Ph}$  the resonance of the CH<sub>2</sub> protons appears as two doublets due to the diastereotopicity of the two



Scheme 1 (i)  $\text{R}''\text{C}\equiv\text{CR}''$  (4 equivalents),  $\text{CHCl}_3$ , reflux

Table 1 Most relevant <sup>1</sup>H NMR chemical shifts ( $\delta$ )<sup>a</sup> for the complexes:  $[\text{Pd}\{[(\text{R}''\text{C}=\text{CR}'')_2(\eta^5\text{-C}_5\text{H}_3\text{CR}=\text{NR}')]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}\text{Cl}]$

Compound	C <sub>5</sub> H <sub>5</sub>	H <sup>3</sup>	H <sup>4b</sup>	H <sup>5</sup>	—CH <sub>2</sub> — <sup>c</sup>	CH=N	—CMe=N
$[\text{Pd}\{[(\text{EtC}=\text{CEt})_2(\eta^5\text{-C}_5\text{H}_3\text{CH}=\text{NCH}_2\text{Ph})]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}\text{Cl}]$ <b>4a</b>	4.11	4.39	4.49	4.44	5.47 4.78	7.87	—
$[\text{Pd}\{[(\text{EtC}=\text{CEt})_2(\eta^5\text{-C}_5\text{H}_3\text{CH}=\text{NCH}_2\text{CH}_2\text{Ph})]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}\text{Cl}]$ <b>4b</b>	4.23	4.42	4.37	4.50	<i>d</i>	7.72	—
$[\text{Pd}\{[(\text{EtC}=\text{CEt})_2(\eta^5\text{-C}_5\text{H}_3\text{CPh}=\text{NCH}_2\text{Ph})]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}\text{Cl}]$ <b>4c</b>	4.20	3.90	4.35	4.86	5.62 4.56	—	—
$[\text{Pd}\{[(\text{EtC}=\text{CEt})_2(\eta^5\text{-C}_5\text{H}_3\text{CMe}=\text{NCH}_2\text{Ph})]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}\text{Cl}]$ <b>4d</b>	4.15	4.39	4.52	4.60	5.88 5.09	—	2.23
$[\text{Pd}\{[(\text{PhC}=\text{CPh})_2(\eta^5\text{-C}_5\text{H}_3\text{CH}=\text{NCH}_2\text{Ph})]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}\text{Cl}]$ <b>5a</b>	4.15	4.37	4.66	4.61	5.45 4.56	7.89	—
$[\text{Pd}\{[(\text{PhC}=\text{CPh})_2(\eta^5\text{-C}_5\text{H}_3\text{CH}=\text{NCH}_2\text{CH}_2\text{Ph})]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}\text{Cl}]$ <b>5b</b>	4.25	4.40	4.35	4.56	<i>d</i>	7.75	—
$[\text{Pd}\{[(\text{PhC}=\text{CPh})_2(\eta^5\text{-C}_5\text{H}_3\text{CPh}=\text{NCH}_2\text{Ph})]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}\text{Cl}]$ <b>5c</b>	4.33	3.63	4.42	4.56	5.32 4.78	—	—
$[\text{Pd}\{[(\text{PhC}=\text{CPh})_2(\eta^5\text{-C}_5\text{H}_3\text{CMe}=\text{NCH}_2\text{Ph})]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}\text{Cl}]$ <b>5d</b>	4.24	4.34	4.52	4.60	5.90 4.10	—	2.24

<sup>a</sup> Labelling refers to the diagram above. <sup>b</sup> Triplet. <sup>c</sup> Doublet of doublets, except as noted. <sup>d</sup> Complex multiplets. <sup>e</sup> Data from ref. 13.

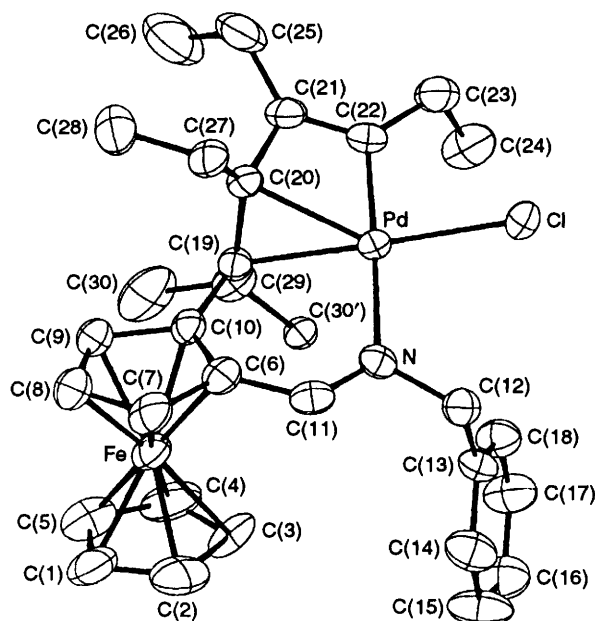


Fig. 2 Molecular structure and atom labelling scheme for  $[\text{Pd}\{[(\text{EtC}=\text{CEt})_2(\eta^5\text{-C}_5\text{H}_3\text{CH}=\text{NCH}_2\text{Ph})]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}\text{Cl}]$  **4a**

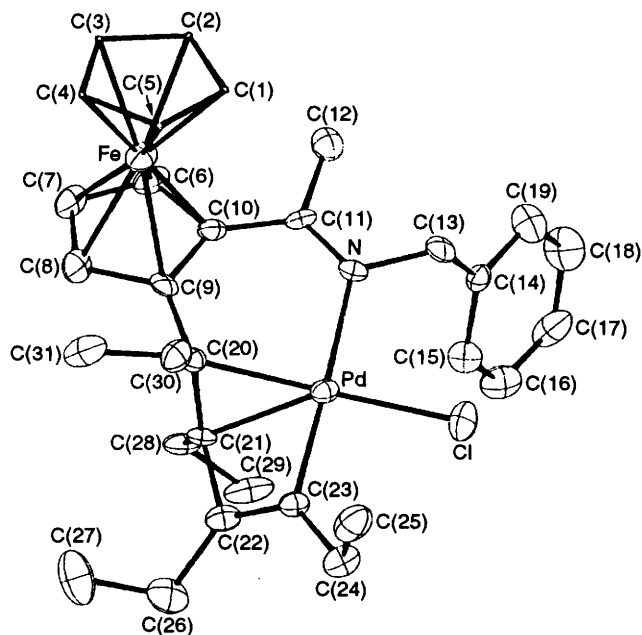


Fig. 3 Molecular structure and atom labelling scheme for  $[\text{Pd}\{[(\text{EtC}=\text{CEt})_2(\eta^5\text{-C}_5\text{H}_3\text{CMe}=\text{NCH}_2\text{Ph})]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}\text{Cl}]$  **4d**. The  $\text{C}(1')\text{-C}(5')$  orientation of the unsubstituted  $\text{C}_5\text{H}_5$  ring is shown

hydrogens in the moiety, while for complexes **4b** and **5b** four multiplets were observed for the two  $\text{CH}_2$  moieties.

Compounds  $[\text{Pd}\{[(\text{EtC}=\text{CEt})_2(\eta^5\text{-C}_5\text{H}_3\text{CR}=\text{NCH}_2\text{Ph})]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}\text{Cl}]$  with  $\text{R} = \text{H}$  **4a** or  $\text{Me}$  **4d** have also been characterized structurally. Perspective drawings of these molecular structures, including their atom labelling schemes, are presented in Figs. 2 and 3, respectively. Final atomic coordinates for non-hydrogen atoms are presented in Tables 2 and 3.

These structures consist of discrete molecules of  $[\text{Pd}\{[(\text{EtC}=\text{CEt})_2(\eta^5\text{-C}_5\text{H}_3\text{CH}=\text{NCH}_2\text{Ph})]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}\text{Cl}]$  **4a** or  $[\text{Pd}\{[(\text{EtC}=\text{CEt})_2(\eta^5\text{-C}_5\text{H}_3\text{C}(\text{Me})=\text{NCH}_2\text{Ph})]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}\text{Cl}]$  **4d**, separated by van der Waals forces. In each the palladium atom is effectively four-co-ordinated, since it is

Table 2 Final atomic coordinates with estimated standard deviations (e.s.d.s) in parentheses for non-hydrogen atoms ( $\times 10^4$  except Pd,  $\times 10^5$ ) in  $[\text{Pd}\{[(\text{EtC}=\text{CEt})_2(\eta^5\text{-C}_5\text{H}_3\text{CH}=\text{NCH}_2\text{Ph})]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}\text{Cl}]$  **4a**

Atom	X/a	Y/b	Z/c
Pd	15 205(2)	16 878(5)	18 197(3)
Fe	1 471(1)	-1 211(1)	3 470(1)
Cl	1 819(1)	2 080(2)	1 008(1)
N	2 048(2)	136(5)	2 384(4)
C(1)	1 357(6)	-2 838(10)	3 802(7)
C(2)	1 599(5)	-2 952(10)	3 407(10)
C(3)	1 231(8)	-2 475(12)	2 587(9)
C(4)	776(5)	-2 063(10)	2 536(8)
C(5)	864(5)	-2 266(11)	3 270(9)
C(6)	1 998(3)	-46(7)	3 538(5)
C(7)	2 223(4)	-514(8)	4 346(5)
C(8)	1 872(4)	-230(9)	4 530(5)
C(9)	1 419(4)	415(8)	3 858(5)
C(10)	1 501(3)	556(7)	3 229(4)
C(11)	2 212(3)	-332(7)	3 083(5)
C(12)	2 257(3)	-482(7)	1 970(5)
C(13)	1 845(3)	-1 385(7)	1 372(5)
C(14)	1 949(4)	-2 574(9)	1 542(6)
C(15)	1 580(4)	-3 445(8)	1 046(7)
C(16)	1 097(4)	-3 116(10)	318(7)
C(17)	965(4)	-1 951(9)	120(6)
C(18)	1 346(3)	-1 099(8)	648(5)
C(19)	1 166(3)	1 367(7)	2 498(4)
C(20)	1 344(3)	1 261(7)	2 627(4)
C(21)	1 020(4)	3 457(7)	1 948(6)
C(22)	1 032(3)	3 090(7)	1 332(5)
C(23)	773(5)	3 649(9)	490(6)
C(24)	367(4)	2 834(10)	-224(6)
C(25)	793(5)	4 558(10)	2 039(7)
C(26)	314(8)	4 386(13)	2 015(13)
C(27)	1 843(4)	2 989(8)	3 475(6)
C(28)	1 715(6)	3 395(12)	4 044(8)
C(29)	581(3)	1 011(8)	1 839(5)
C(30)	436(6)	2 439(13)	1 159(8)
C(30')	258(8)	798(25)	2 137(16)

bound to a chlorine, the nitrogen atom, the terminal carbon atom of the  $\eta^3$ -butadienyl fragment [C(22) in **4a**, C(23) in **4d**] and the middle point of the segment defined by the atoms C(19) and C(20) in **4a**, or C(20) and C(21) in **4d** (hereafter referred to as X and X' respectively) (Figs. 2 and 3, Table 4). A slightly distorted square-planar environment is the result. Selected bond lengths and angles for the two crystal structures are presented in Tables 4, 5 and 6.

In the two compounds the Pd-Cl bond lengths [2.357(4) Å (**4a**) and 2.342(2) Å (**4d**)] are similar to that found for complex **5a**,<sup>13</sup> and clearly larger than the values reported for related five-membered metallocycles with  $\sigma(\text{Pd}-\text{C}_{\text{sp}^2}, \text{ferrocene})$  bonds.<sup>10,12-17</sup>

These complexes contain a bicyclic system, which is formed by the fusion of the 1,2-disubstituted pentagonal ring of the ferrocenyl moiety and a nine-membered metallocycle (Figs. 2 and 3). The iminic group is contained within the nine-membered metallocycle and the C=N bond length [1.289(12) Å in **4a** and 1.308(9) Å in **4d**], is clearly longer than those found in related ferrocenylimines {ca. 1.24-1.26 Å},<sup>10b,11</sup> in particular that for the free ligand  $[(\eta^5\text{-C}_5\text{H}_4\text{CH}=\text{NCH}_2\text{Ph})\text{Fe}(\eta^5\text{-C}_5\text{H}_5)]$  [1.262(7) Å].<sup>11</sup> The angle formed by the plane defined by the pentagonal ring of the ferrocenyl moiety and the iminic group [C(10), C(11), N in **4a** and C(6), C(11), N in **4d**] is clearly larger than in the free ligands<sup>10b,11</sup> and related cyclopalladated derivatives  $[\text{Pd}\{(\eta^5\text{-C}_5\text{H}_3\text{CR}=\text{NR}')\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}\text{Cl}(\text{PPh}_3)]$ <sup>10</sup> ( $\text{R} = \text{H}$  or  $\text{Me}$ ), thus showing the distortion introduced by the formation of the nine-membered metallocycle. In both cases the ligands retain the *anti* conformation as reflected in the

**Table 3** Final atomic coordinates with e.s.d.s in parentheses for non-hydrogen atoms ( $\times 10^4$ ) in  $[\text{Pd}\{[(\text{EtC}=\text{CEt})_2(\eta^5\text{-C}_5\text{H}_3\text{CMe}=\text{NCH}_2\text{Ph})]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}\}] \mathbf{4d}$ 

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Pd	2103(1)	268(1)	3118(1)	C(12)	970(4)	-1654(8)	5731(6)
Fe	318(1)	-2484(1)	3028(1)	C(13)	2249(4)	-917(6)	5408(6)
Cl	3191(1)	418(2)	3784(2)	C(14)	2234(4)	24(7)	6282(7)
N	1759(3)	-728(5)	4532(5)	C(15)	2195(4)	1226(8)	6063(7)
C(1)	999(7)	-3864(15)	3339(18)	C(16)	2186(4)	2074(9)	6871(8)
C(2)	402(14)	-4104(15)	3854(8)	C(17)	2217(5)	1735(10)	7923(8)
C(3)	-114(5)	-4149(15)	3062(22)	C(18)	2244(5)	529(11)	8128(7)
C(4)	164(11)	-3938(15)	2058(12)	C(19)	2258(5)	-323(9)	7325(7)
C(5)	852(10)	-3761(15)	2229(15)	C(20)	1202(3)	-178(6)	2162(6)
C(1')	777(13)	-3981(17)	3672(13)	C(21)	1253(4)	1092(6)	2248(6)
C(2')	85(13)	-4169(17)	3629(18)	C(22)	1751(4)	1751(7)	1592(6)
C(3')	-137(6)	-4097(17)	2547(25)	C(23)	2337(4)	1299(7)	1880(6)
C(4')	417(14)	-3864(17)	1920(7)	C(24)	2992(4)	1592(8)	1468(8)
C(5')	982(6)	-3792(16)	2616(21)	C(25)	3328(5)	493(9)	977(8)
C(6)	-53(4)	-1294(7)	4078(8)	C(26)	1544(5)	2757(8)	832(8)
C(7)	-417(4)	-1221(7)	3127(8)	C(27)	993(5)	2409(11)	70(9)
C(8)	9(4)	-872(7)	2306(7)	C(28)	780(4)	1846(7)	2865(7)
C(9)	656(4)	-731(6)	2763(6)	C(29)	1108(5)	2878(8)	3619(8)
C(10)	624(4)	-1009(6)	3884(6)	C(30)	1457(4)	-906(8)	1221(7)
C(11)	1159(4)	-1091(6)	4702(6)	C(31)	967(5)	-1146(9)	340(7)

**Table 4** Selected bond lengths (in Å) for

$[\text{Pd}\{[(\text{EtC}=\text{CEt})_2(\eta^5\text{-C}_5\text{H}_3\text{CR}=\text{NCH}_2\text{Ph})]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}\}]$  (R = H **4a** or Me **4d**) with e.s.d.s in parentheses

Compound <b>4a</b>		Compound <b>4d</b>	
Cl-Pd	2.357(4)	N-Pd	2.187(6)
C(19)-Pd	2.236(11)	C(20)-Pd	2.237(10)
X <sup>a</sup> -Pd	2.121(10)	C(21)-Pd	2.633(10)
C(22)-Pd	1.990(7)	Fe-C <sup>b</sup>	2.044(13)
C(11)-N	1.289(12)	C(12)-N	1.499(14)
C(19)-C(10)	1.497(10)	C(13)-C(12)	1.503(10)
C(14)-C(13)	1.378(13)	C(18)-C(13)	1.372(9)
C(15)-C(14)	1.375(13)	C(16)-C(15)	1.366(12)
C(17)-C(16)	1.366(15)	C(18)-C(17)	1.389(12)
C(20)-C(19)	1.422(11)	C(29)-C(19)	1.508(10)
C(21)-C(20)	1.499(11)	C(27)-C(20)	1.530(10)
C(22)-C(21)	1.332(17)	C(25)-C(21)	1.493(17)
C(23)-C(22)	1.512(14)	C(24)-C(23)	1.520(13)
C(26)-C(25)	1.457(32)	C(28)-C(27)	1.495(24)
C(30)-C(29)	1.449(18)	C(30')-C(29)	1.461(38)
Cl-Pd	2.342(2)	N-Pd	2.225(6)
C(20)-Pd	2.208(7)	C(21)-Pd	2.207(7)
X <sup>c</sup> -Pd	2.092(8)	C(22)-Pd	2.605(8)
C(23)-Pd	2.000(8)	Fe-C <sup>b</sup>	2.064(21)
C(11)-C(10)	1.473(10)	C(11)-N	1.308(9)
C(12)-C(11)	1.497(10)	C(13)-N	1.471(9)
C(14)-C(13)	1.516(11)	C(15)-C(14)	1.361(10)
C(16)-C(15)	1.385(12)	C(17)-C(16)	1.373(13)
C(18)-C(17)	1.361(14)	C(19)-C(18)	1.383(13)
C(19)-C(18)	1.365(11)	C(20)-C(19)	1.495(10)
C(21)-C(20)	1.414(10)	C(22)-C(21)	1.513(10)
C(23)-C(22)	1.329(10)	C(24)-C(23)	1.481(11)
C(25)-C(24)	1.534(12)	C(26)-C(25)	1.518(11)
C(27)-C(26)	1.496(13)	C(28)-C(27)	1.508(10)
C(29)-C(28)	1.543(11)	C(30)-C(29)	1.536(10)
C(31)-C(30)	1.485(11)		

<sup>a</sup> X represents the middle point of the segment defined by the atoms C(19) and C(20) in compound **4a**. <sup>b</sup> Average value. <sup>c</sup> X' represents the middle point of the segment defined by the atoms C(20) and C(21) in complex **4d**.

torsion angles C(6)-C(11)-N-C(12) -168.7° for **4a** and C(10)-C(11)-N-C(13) -177.3° for **4d**.

In the two structures, the double bond of the  $\eta^3$ -butadienyl unit closest to the ferrocenyl group is bound symmetrically to the palladium atom as reflected in the two Pd-C bond distances

**Table 5** Selected bond angles (°) for

$[\text{Pd}\{[(\text{EtC}=\text{CEt})_2(\eta^5\text{-C}_5\text{H}_3\text{CH}=\text{NCH}_2\text{Ph})]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}\}] \mathbf{4a}$  with e.s.d.s in parentheses

N-Pd-Cl	92.0(2)	C(19)-Pd-Cl	175.1(2)
C(19)-Pd-N	92.0(3)	C(20)-Pd-Cl	142.5(2)
C(20)-Pd-N	114.0(3)	C(20)-Pd-C(19)	37.1(3)
C(21)-Pd-Cl	115.0(3)	C(21)-Pd-N	148.6(3)
C(21)-Pd-C(19)	62.1(3)	C(21)-Pd-C(20)	34.6(3)
C(22)-Pd-Cl	90.1(4)	C(22)-Pd-N	177.9(4)
C(22)-Pd-C(19)	86.0(4)	C(22)-Pd-C(20)	64.1(4)
C(22)-Pd-C(21)	29.5(4)	C(11)-N-Pd	125.2(7)
C(12)-N-Pd	121.2(5)	C(12)-N-C(11)	113.6(7)
C(19)-C(10)-C(6)	129.7(10)	C(19)-C(10)-C(9)	123.6(8)
C(14)-C(13)-C(12)	120.6(6)	C(18)-C(13)-C(12)	123.5(7)
C(18)-C(13)-C(14)	116.0(7)	C(15)-C(14)-C(13)	123.7(7)
C(16)-C(15)-C(14)	118.0(9)	C(17)-C(16)-C(15)	121.0(9)
C(18)-C(17)-C(16)	118.9(8)	C(17)-C(18)-C(13)	122.3(8)
C(17)-C(18)-C(13)	122.3(8)	C(10)-C(19)-Pd	113.8(6)
C(20)-C(19)-Pd	71.5(6)	C(20)-C(19)-C(10)	116.3(5)
C(29)-C(19)-Pd	105.6(6)	C(29)-C(19)-C(10)	116.5(7)
C(29)-C(19)-C(20)	122.5(6)	C(19)-C(20)-Pd	71.4(6)
C(29)-C(20)-Pd	87.3(7)	C(21)-C(20)-C(19)	120.4(5)
C(27)-C(20)-Pd	115.6(7)	C(27)-C(20)-C(19)	118.1(7)
C(20)-C(21)-Pd	58.1(5)	C(22)-C(21)-Pd	47.4(4)
C(22)-C(21)-C(20)	105.4(8)	C(25)-C(21)-Pd	172.7(9)
C(25)-C(21)-C(20)	123.6(10)	C(25)-C(21)-C(22)	130.8(9)
C(21)-C(22)-Pd	103.1(6)	C(23)-C(22)-Pd	128.0(9)
C(23)-C(22)-C(21)	128.8(8)	C(24)-C(23)-C(22)	112.5(9)
C(26)-C(25)-C(21)	115.1(11)	C(28)-C(27)-C(20)	113.7(10)
C(30)-C(29)-C(19)	121.0(11)	C(30')-C(29)-C(19)	115.4(11)
C(30')-C(29)-C(30)	113.2(14)		

[2.236(11) and 2.237(10) Å in **4a**, 2.208(7) and 2.207(7) Å in **4d**], which are practically identical (the differences do not exceed  $3\sigma$ ). This arrangement is different from those reported for most of the nine-membered palladacyclic derivatives arising from the insertion of two alkyne molecules.<sup>6,8,9,13</sup> The relative orientation of the four ethyl groups in both cases (Figs. 2 and 3) agrees with the common distribution of the substituents on the alkyne in nine-membered palladacycles arising from bis-(insertion) reactions of alkynes,<sup>6,8,9,13</sup> and provides less steric hindrance between the remaining substituents. The phenyl ring of the benzyl group is practically planar and its orientation is almost perpendicular to that of the  $\text{C}_5\text{H}_3$  ring (92.9° in **4a** and 98.5° in **4d**).

The distance between Fe and Pd is practically identical in the

**Table 6** Selected bond angles (°) for

$[\text{Pd}\{[(\text{EtC}=\text{CEt})_2(\eta^5\text{-C}_5\text{H}_3\text{CMe}=\text{NCH}_2\text{Ph})]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}\text{Cl}]$  **4d**, with e.s.d.s in parentheses

N-Pd-Cl	93.9(2)	C(20)-Pd-Cl	164.5(2)
C(20)-Pd-N	92.7(2)	C(21)-Pd-Cl	149.2(2)
C(21)-Pd-C(20)	37.4(3)	C(21)-Pd-N	109.8(2)
C(22)-Pd-N	144.6(2)	C(22)-Pd-Cl	116.7(2)
C(23)-Pd-N	173.7(3)	C(23)-Pd-C(20)	85.4(3)
C(23)-Pd-C(21)	65.3(3)	C(23)-Pd-Cl	89.5(2)
C(10)-C(11)-C(12)	115.0(6)	N-C(11)-C(10)	122.4(7)
N-C(11)-C(12)	122.5(7)	N-C(13)-C(14)	114.5(6)
C(9)-C(20)-C(21)	115.0(6)	C(9)-C(20)-Pd	115.6(5)
C(30)-C(20)-Pd	104.0(5)	C(22)-C(21)-C(20)	119.1(6)
C(8)-C(9)-C(20)	122.1(7)	C(10)-C(9)-C(20)	129.8(7)
C(6)-C(10)-C(11)	123.7(7)	C(9)-C(10)-C(11)	129.4(7)
C(15)-C(14)-C(19)	118.0(8)	C(15)-C(14)-C(13)	121.9(7)
C(19)-C(14)-C(13)	120.1(7)	C(14)-C(15)-C(16)	121.1(8)
C(17)-C(16)-C(15)	121.3(9)	C(180)-C(17)-C(16)	116.8(9)
C(17)-C(18)-C(19)	122.3(9)	C(14)-C(19)-C(18)	120.5(9)
C(21)-C(20)-C(9)	115.0(6)	C(21)-C(20)-C(30)	123.7(7)
C(9)-C(20)-C(30)	116.7(6)	C(20)-C(21)-C(28)	122.9(6)
C(20)-C(21)-C(22)	119.1(6)	C(28)-C(21)-C(22)	117.5(6)
C(23)-C(22)-C(21)	106.2(7)	C(23)-C(22)-C(26)	132.3(7)
C(21)-C(22)-C(26)	121.4(7)	C(22)-C(23)-C(24)	129.0(8)
C(23)-C(24)-C(25)	112.5(7)	C(27)-C(26)-C(22)	113.4(8)
C(21)-C(28)-C(29)	114.9(7)	C(31)-C(30)-C(20)	115.7(7)

two compounds [4.733(1) Å in **4a**, 4.731(2) Å in **4d**] and is clearly longer than those reported for the cyclopalladated derivatives containing five-membered palladacycles with  $\sigma(\text{Pd}-\text{C}_{\text{sp}^2, \text{ferrocene}})$  bonds (3.58–3.59 Å).<sup>10,12,14–17</sup>

The Fe–C(ring) bond lengths range from 2.029(10) to 2.073(8) Å in **4a** and from 2.027(8) to 2.090(7) Å in **4d**. The minimum and maximum values involve the two carbon atoms shared by the nine-membered metallacycle and the pentagonal C<sub>5</sub>H<sub>3</sub> ring. This type of distortion has also been observed in the crystal structures of monomeric cyclopalladated derivatives of general formula:  $[\text{Pd}\{(\eta^5\text{-C}_5\text{H}_3\text{CR}=\text{NR}')\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}\text{-Cl}(\text{PR}'_3)]$  (R = H, R' = CH<sub>2</sub>Ph, R'' = Ph; R = Me, R' = CH<sub>2</sub>CH<sub>2</sub>Ph, R'' = Ph; R = R' = R'' = Ph).<sup>10,12</sup>

In complex **4a**, the two rings of the ferrocenyl moiety are nearly parallel and their relative orientation is intermediate between the ideal eclipsed and staggered conformations [the average value for the twist angle<sup>18</sup> is –14.9(5)°], while for **4d** two different orientations of the unsubstituted C<sub>5</sub>H<sub>5</sub> ring were found.

Previous studies on cyclopalladated compounds derived from ferrocene have shown that the susceptibility of these compounds to oxidation depends on the substituents.<sup>12,19</sup> Electrochemical studies were undertaken on some of the bis(insertion) products in order to elucidate the influence of the incorporation of a  $\eta^3$ -butadienyl fragment linked to the palladium, on the oxidation potential of the iron(II).

Cyclic voltammograms of these complexes exhibit an anodic process with a directly associated reduction in the reverse scan. The experiments were carried out using different scan rates,  $v$  (0.05–1.00 mV s<sup>-1</sup>) and in all cases  $i_{\text{pa}}/i_{\text{pc}} = 1$  with a linear relationship between  $i_{\text{pa}}$  and  $v^{1/2}$  indicating a simple and reversible one-electron transfer process.<sup>20</sup> However, the peak-to-peak separation,  $\Delta E$ , increased progressively from 0.07 to 0.17 V. It is well known that the trend of  $\Delta E$  with scan rate can give information on the extent of the structural reorganization accompanying redox change.<sup>21</sup> For the compounds reported here the  $\Delta E$  values depart appreciably from the constant value of 0.059 V (theoretically expected for an electrochemically reversible one-electron step oxidation–reduction process<sup>20</sup>), suggesting structural reorganization takes place on oxidation; we will return to this point later.

Table 7 shows the half-wave potentials  $E_{1/2}$  obtained from

cyclic voltammeteries for the compounds under study, the free ligands and several five-membered cyclopalladated complexes containing a  $\sigma(\text{Pd}-\text{C}_{\text{sp}^2, \text{ferrocene}})$  bond. In all cases, the  $E_{1/2}$  values obtained for the double insertion derivatives are higher than those reported for the ferrocenyl Schiff bases and their cyclopalladated derivatives,<sup>12</sup> thus indicating that the formation of the nine-membered metallacycle clearly inhibits the oxidation of the iron centre. From electrochemical studies on ferrocene derivatives, it is accepted that the  $E_{1/2}$  values are clearly dependent on the nature of the substituent.<sup>21–23</sup> In general, higher values are found for derivatives containing strong electron-withdrawing groups, while electron-donor substituents facilitate the oxidation of the iron centre (as reflected in their  $E_{1/2}$  values which are more cathodic than that of ferrocene). Consequently, in compounds **4** and **5** the substituents in the ferrocenyl moiety appear at first sight to have a stronger electron withdrawing ability than aldehyde or ketone groups in ferrocenecarbaldehyde ( $E_{1/2} = 0.24$  V) and acetylferrocene ( $E_{1/2} = 0.22$  V).<sup>24</sup> However, it must be stated that for the nine-membered metallacycle the oxidation is from the highest occupied molecular orbital (HOMO) which may not be solely iron based. In addition, as explained above, there is reason to believe that structural reorganization takes place on oxidation. So comparison to the uncomplexed ferrocenyl ligands is not straightforward. It is therefore necessary to use a technique capable of sampling the iron atoms directly, to understand the nature of their role.

In order to confirm the effect of the substituents in the bis(insertion) products upon the iron centre, Mössbauer spectra of complexes **4a** and **4d** were recorded at 78 K. In both cases the spectra consist of a single quadrupolar doublet. The isomer shifts (i.s.) are consistent with those obtained for ferrocenyl Schiff bases<sup>11,12,25</sup> and related cyclopalladated derivatives<sup>11,12</sup> (Table 8).

The quadrupolar splitting parameters,  $q.s.$ , for **4a** and **4d** (Table 8) are larger than those found in five-membered cyclopalladated derivatives<sup>11,12</sup> containing a  $\sigma(\text{Pd}-\text{C}_{\text{sp}^2, \text{ferrocene}})$  bond and a ferrocenyl Schiff base as ligand, thus demonstrating that the  $\eta^3$ -butadienyl unit satisfies the electron withdrawing effect of the palladium atom and shields the ferrocenyl group. Furthermore, previous studies on Mössbauer spectra of related cyclopalladated compounds<sup>12</sup> have shown that the difference  $\Delta - 0.02$  where  $\Delta = q.s._{\text{free ligand}} - q.s._{\text{complex}}$  can be used as a measure of the electron density withdrawn by the palladium atom through the iminic nitrogen. The application of this criterion to compound **4a** allows us to conclude that the bis(olefin) unit bound to the ferrocenyl group satisfies the needs of the palladium atom, since the difference  $\Delta - 0.02$  mm s<sup>-1</sup> is practically zero. Thus the high  $q.s.$  values obtained for complexes **4a** and **4d** can be explained in terms of no further  $\pi$ -conjugation between the C=N and the C<sub>5</sub>H<sub>3</sub> ring, on metal complexation compared to the parent ligand, and little or no interaction of the latter with the  $\eta^3$ -butadienyl unit in the structure before oxidation.

In conclusion, the  $q.s.$  values for **4a** and **4d** are also larger than in ferrocenecarbaldehyde ( $q.s. = 2.24$  mm s<sup>-1</sup>) and acetylferrocene ( $q.s. = 2.27$  mm s<sup>-1</sup>).<sup>11,26</sup> These findings are not consistent with the results obtained from the electrochemical studies described above as we would expect low  $E_{1/2}$  values for such  $q.s.$  values. These results reveal that the environment of the iron(II) in the bis(insertion) derivatives is not like that found for the aldehyde or ketone but more like the ferrocenylimines. The most likely explanations are either (a) that structural changes occur on or during oxidation and hinder the process so that the resulting oxidation potentials do not reflect the initial iron(II) environment or (b) that the HOMO is indeed not solely iron based.

*The Effect of the Chelate Ligand on the Insertion Reaction.*—As mentioned above, although it has been possible to isolate and characterize compounds  $[\text{Pd}\{[(\text{R}''\text{C}=\text{CR}'')_2(\eta^5\text{-C}_5\text{H}_3\text{CR}=\text{N}-$

**Table 7** Half-wave potentials  $E_{1/2}^a$ /V for the bis(insertion) complexes, free ligands, and dinuclear five-membered cyclopalladated derivatives

	$E_{1/2}^a$	Ref.
Monomeric nine-membered metallacycles		
$[\text{Pd}\{(\text{EtC}=\text{CEt})_2(\eta^5\text{-C}_5\text{H}_3\text{CH}=\text{NCH}_2\text{Ph})\}\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}]$ <b>4a</b>	0.34	<i>b</i>
$[\text{Pd}\{(\text{PhC}=\text{CPh})_2(\eta^5\text{-C}_5\text{H}_3\text{CH}=\text{NCH}_2\text{Ph})\}\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}]$ <b>5a</b>	0.32	<i>b</i>
$[\text{Pd}\{(\text{EtC}=\text{CEt})_2(\eta^5\text{-C}_5\text{H}_3\text{CMe}=\text{NCH}_2\text{Ph})\}\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}]$ <b>4d</b>	0.32	<i>b</i>
$[\text{Pd}\{(\text{PhC}=\text{CPh})_2(\eta^5\text{-C}_5\text{H}_3\text{CMe}=\text{NCH}_2\text{Ph})\}\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}]$ <b>5d</b>	0.30	<i>b</i>
Free ligands		
$[(\eta^5\text{-C}_5\text{H}_4\text{CH}=\text{NCH}_2\text{Ph})\text{Fe}(\eta^5\text{-C}_5\text{H}_5)]$ <b>1a</b>	0.13	12
$[(\eta^5\text{-C}_5\text{H}_4\text{CH}=\text{NCH}_2\text{CH}_2\text{Ph})\text{Fe}(\eta^5\text{-C}_5\text{H}_5)]$ <b>1b</b>	0.12	<i>b</i>
$[(\eta^5\text{-C}_5\text{H}_4\text{CPh}=\text{NCH}_2\text{Ph})\text{Fe}(\eta^5\text{-C}_5\text{H}_5)]$ <b>1c</b>	0.13	<i>b</i>
$[(\eta^5\text{-C}_5\text{H}_4\text{CMe}=\text{NCH}_2\text{Ph})\text{Fe}(\eta^5\text{-C}_5\text{H}_5)]$ <b>1d</b>	0.06	<i>b</i>
$[(\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{NMe}_2)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)]$	-0.01	12
Di- $\mu$ -chloro-bridged five-membered metallacycles		
$[\{\text{Pd}[(\eta^5\text{-C}_5\text{H}_3\text{CH}=\text{NCH}_2\text{Ph})\text{Fe}(\eta^5\text{-C}_5\text{H}_5)](\mu\text{-Cl})\}_2]$ <b>2a</b>	0.06	<i>b</i>
$[\{\text{Pd}[(\eta^5\text{-C}_5\text{H}_3\text{CH}=\text{NCH}_2\text{CH}_2\text{Ph})\text{Fe}(\eta^5\text{-C}_5\text{H}_5)](\mu\text{-Cl})\}_2]$ <b>2b</b>	0.05	<i>b</i>
$[\{\text{Pd}[(\eta^5\text{-C}_5\text{H}_3\text{CPh}=\text{NCH}_2\text{Ph})\text{Fe}(\eta^5\text{-C}_5\text{H}_5)](\mu\text{-Cl})\}_2]$ <b>2c</b>	0.06	<i>b</i>
$[\{\text{Pd}[(\eta^5\text{-C}_5\text{H}_3\text{CMe}=\text{NCH}_2\text{Ph})\text{Fe}(\eta^5\text{-C}_5\text{H}_5)](\mu\text{-Cl})\}_2]$ <b>2d</b>	0.03	<i>b</i>
$[\{\text{Pd}[(\eta^5\text{-C}_5\text{H}_3\text{CH}_2\text{NMe}_2)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)](\mu\text{-Cl})\}_2]$ <b>2e</b>	-0.08	12

<sup>a</sup> Uncertainty in  $E_{1/2} = \pm 5 \times 10^{-3}$  V. <sup>b</sup> This work.

**Table 8** Mössbauer parameters: isomer shift (i.s.)<sup>a</sup> and quadrupole splitting (q.s.)<sup>a</sup> for some ferrocenyl Schiff bases and related nine-membered cyclopalladated complexes. Data for five-membered metallacycles related to complexes **2a–2e** are also included, in these cases the compound relationship and expected q.s. values if ligands on palladium are a chlorine and a triphenylphosphine are also indicated under the labelling (q.s.)<sup>c</sup>

Schiff bases		i.s.	q.s.	Ref.
$[(\eta^5\text{-C}_5\text{H}_4\text{CH}=\text{NCH}_2\text{Ph})\text{Fe}(\eta^5\text{-C}_5\text{H}_5)]$		0.54(1)	2.29(1)	11
$[(\eta^5\text{-C}_5\text{H}_4\text{CH}=\text{NCH}_2\text{CH}_2\text{Ph})\text{Fe}(\eta^5\text{-C}_5\text{H}_5)]$		0.44(1)	2.34(1)	10a
$[(\eta^5\text{-C}_5\text{H}_4\text{CPh}=\text{NCH}_2\text{Ph})\text{Fe}(\eta^5\text{-C}_5\text{H}_5)]$		0.54(1)	2.35(1)	11
$[(\eta^5\text{-C}_5\text{H}_4\text{CPh}=\text{NCH}_2\text{C}_6\text{H}_4\text{Cl-2})\text{Fe}(\eta^5\text{-C}_5\text{H}_5)]$		0.54(1)	2.35(1)	11
$[(\eta^5\text{-C}_5\text{H}_4\text{CPh}=\text{NCH}_2\text{C}_6\text{H}_4\text{Me-2})\text{Fe}(\eta^5\text{-C}_5\text{H}_5)]$		0.52(1)	2.29(1)	11
Monomeric nine-membered metallacycles				
$[\text{Pd}\{(\text{EtC}=\text{CEt})_2[(\eta^5\text{-C}_5\text{H}_3\text{CH}=\text{NCH}_2\text{Ph})\text{Fe}(\eta^5\text{-C}_5\text{H}_5)]\}\text{Cl}]$		0.51(1)	2.31(1)	This work
$[\text{Pd}\{(\text{EtC}=\text{CEt})_2[(\eta^5\text{-C}_5\text{H}_3\text{CMe}=\text{NCH}_2\text{Ph})\text{Fe}(\eta^5\text{-C}_5\text{H}_5)]\}\text{Cl}]$		0.51(1)	2.32(1)	This work
Monomeric five-membered metallacycles				
$[\text{Pd}\{(\eta^5\text{-C}_5\text{H}_3\text{CH}=\text{NCH}_2\text{Ph})\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}\text{Cl}(\text{mim})]$ <sup>b</sup>	Relationship to <b>2a</b>	0.52(1)	2.24(1)	(q.s.) <sup>c</sup> 2.22(1) 12
$[\text{Pd}\{(\eta^5\text{-C}_5\text{H}_3\text{CMe}=\text{NCH}_2\text{Ph})\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}\text{Cl}(\text{PPh}_3)]$ <sup>c</sup>	<b>2b</b>	0.45	2.16	2.16 10a
$[\text{Pd}\{(\eta^5\text{-C}_5\text{H}_3\text{CMe}=\text{NCH}_2\text{CH}_2\text{Ph})\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}\text{Cl}(\text{PEt}_3)]$ <sup>c</sup>	<b>2b</b>	0.44	2.21	2.16 10a
$[\text{Pd}\{(\eta^5\text{-C}_5\text{H}_3\text{CPh}=\text{NCH}_2\text{C}_6\text{H}_4\text{Cl-2})\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}\text{Cl}(\text{PPh}_3)]$ <sup>d</sup>	<b>2c</b>	0.52(1)	2.22(1)	2.22(1) 11
$[\text{Pd}\{(\eta^5\text{-C}_5\text{H}_3\text{CPh}=\text{NCH}_2\text{C}_6\text{H}_4\text{Me-2})\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}\text{Cl}(\text{PPh}_3)]$ <sup>d</sup>	<b>2c</b>	0.52(1)	2.21(1)	2.21(1) 11
$[\text{Pd}\{(\eta^5\text{-C}_5\text{H}_3\text{CMe}=\text{NCH}_2\text{Ph})\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}\text{Cl}(\text{PPh}_3)]$	<b>2d</b>	0.54(1)	2.23(1)	2.23(1) 11
$[\text{Pd}\{(\eta^5\text{-C}_5\text{H}_3\text{CH}_2\text{NMe}_2)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}\text{Cl}(\text{mim})]$	<b>2e</b>	0.54(1)	2.41(1)	2.39(1) 12
$[\text{Pd}\{(\eta^5\text{-C}_5\text{H}_3\text{CH}_2\text{NMe}_2)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}\text{Cl}(\text{PPh}_3)]$	<b>2e</b>	0.53(1)	2.39(1)	2.39(1) 12

<sup>a</sup> In  $\text{mm s}^{-1}$ . <sup>b</sup> mim = 1-methylimidazole. <sup>c</sup> Data from ref. 11, and in this case the spectrum was recorded at 298 K. <sup>d</sup> These values are for compounds containing  $\text{CH}_2\text{C}_6\text{H}_4\text{Cl-2}$  and  $\text{CH}_2\text{C}_6\text{H}_4\text{Me-2}$  bound to the iminic nitrogen, but they are expected to be similar to those of the analogous derivatives with a  $\text{CH}_2\text{Ph}$  group.

$\text{R}')\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}]$  [ $\text{R}'' = \text{Et}$  (**4a–4d**) or  $\text{Ph}$  (**5a–5d**)], from  $[\{\text{Pd}[(\eta^5\text{-C}_5\text{H}_3\text{C}(\text{R})=\text{NR}')\text{Fe}(\eta^5\text{-C}_5\text{H}_5)](\mu\text{-Cl})\}_2]$  **2a–2d**, some differences in the reactivity of the di- $\mu$ -chloro-bridged derivatives were observed.

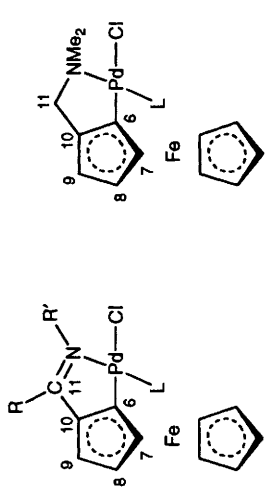
When the reactions were carried out at room temperature for 1 h using  $\text{CH}_2\text{Cl}_2$  or  $\text{CHCl}_3$  as solvent, the starting materials were recovered and no evidence of the formation of the corresponding mono- or bis-(insertion) products (**4**, **5a–5d**) was detected, showing that compounds **2a–2d** are clearly less reactive than  $[\{\text{Pd}[(\eta^5\text{-C}_5\text{H}_3\text{CH}_2\text{NMe}_2)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)](\mu\text{-Cl})\}_2]$  **2e**, which undergoes double insertion of the alkyne even at room temperature.<sup>8</sup> Complexes **4a–4c** and **5a–5c** (Scheme 1)

were easily prepared under more forcing experimental conditions (refluxing  $\text{CHCl}_3$  for 1.5 h). However, when the reaction was carried out using  $[\{\text{Pd}[(\eta^5\text{-C}_5\text{H}_3\text{CMe}=\text{NCH}_2\text{-Ph})\text{Fe}(\eta^5\text{-C}_5\text{H}_5)](\mu\text{-Cl})\}_2]$  **2d**, as starting material, palladium metal was obtained, and the synthesis of the bis(insertion) complexes (**4d**, **5d**) was achieved only when shorter reaction times were used (*ca.* 45 min). Under these conditions, the yield of the reaction was similar to those obtained for  $[\{\text{Pd}[(\text{R}''\text{C}=\text{CR}')_2(\eta^5\text{-C}_5\text{H}_3\text{CR}=\text{NR}')\text{Fe}(\eta^5\text{-C}_5\text{H}_5)](\mu\text{-Cl})\}_2]$  ( $\text{R} = \text{H}$  or  $\text{Ph}$ ,  $\text{R}' = \text{CH}_2\text{Ph}$  or  $\text{CH}_2\text{CH}_2\text{Ph}$ ,  $\text{R}'' = \text{Et}$  or  $\text{Ph}$ ). Compounds **4a–4c** and **5a–5c** were also obtained using shorter reaction times (from 40 min to 1 h), but in these cases

**Table 9** Bond lengths (Å) and angles (°) of the metallacycle in five-membered cyclopalladated complexes containing a  $\sigma(\text{Pd}-\text{C}_{\text{sp}^2}, \text{ferrocene})$  bond. Labelling of the atoms as in the diagram below, e.s.d.s are given in parentheses

Compound	Pd-C(6)	C(6)-C(10)	C(10)-C(11)	C(11)-N	N-Pd	Pd-C(6)-C(10)	C(6)-C(10)-C(11)	C(10)-C(11)-N	C(11)-N-Pd	N-Pd-C(6)
$[\text{Pd}\{\{\eta^5\text{-C}_3\text{H}_5\text{CH}_2\text{NMe}_2\}\text{Fe}(\eta^5\text{-C}_3\text{H}_5)\}\text{Cl}(\text{py})]^\text{a}$	1.949(5)	1.456(7)	1.491(7)	1.486(7)	2.123(5)	114.0(3)	119.5(4)	108.3(4)	112.8(3)	82.9(2)
$[\text{Pd}\{\{\eta^5\text{-C}_3\text{H}_5\text{CH}_2\text{NMe}_2\}\text{Fe}(\eta^5\text{-C}_3\text{H}_5)\}\text{Cl}(\text{mim})]^\text{b}$	1.967(3)	1.429(5)	1.495(5)	1.526(5)	2.112(3)	114.2(2)	120.1(3)	108.8(3)	112.5(2)	83.5(1)
$[\text{Pd}\{\{\eta^5\text{-C}_3\text{H}_5\text{CMe}=\text{NCH}_2\text{CH}_2\text{Ph}\}\text{Fe}(\eta^5\text{-C}_3\text{H}_5)\}\text{Cl}(\text{PPh}_3)]^\text{c}$	1.984(6)	1.428(11)	1.418(11)	1.305(9)	2.130(6)	111.0(5)	119.3(6)	114.7(7)	113.6(5)	80.8(3)
$[\text{Pd}\{\{\eta^5\text{-C}_3\text{H}_5\text{CPh}=\text{NPh}\}\text{Fe}(\eta^5\text{-C}_3\text{H}_5)\}\text{Cl}(\text{PPh}_3)]^\text{d}$	1.997(5)	1.432(7)	1.438(8)	1.308(7)	2.111(4)	111.7(3)	118.7(4)	113.8(4)	115.3(3)	80.4(2)
$[\text{Pd}\{\{\eta^5\text{-C}_3\text{H}_5\text{CH}=\text{NCH}_2\text{CH}_2\text{Ph}\}\text{Fe}(\eta^5\text{-C}_3\text{H}_5)\}\text{Cl}(\text{PEt}_3)]^\text{e}$	1.999(6)	1.434(9)	1.467(9)	1.280(8)	2.148(5)	111.9(3)	116.9(8)	117.0(7)	112.9(3)	80.8(3)
$[\text{Pd}\{\{\eta^5\text{-C}_3\text{H}_5\text{CH}=\text{NCH}_2\text{Ph}\}\text{Fe}(\eta^5\text{-C}_3\text{H}_5)\}\text{Cl}(\text{PPh}_3)]^\text{b}$	2.005(5)	1.430(9)	1.475(9)	1.279(7)	2.146(6)	111.5(2)	118.0(3)	115.2(3)	114.3(2)	80.8(2)

<sup>a</sup> Data from ref. 14. <sup>b</sup> Data from ref. 10b. <sup>c</sup> Data from ref. 10c. <sup>d</sup> Data from ref. 10a.



the yields of the reactions decreased considerably (*ca.* 25–45%) and unreacted di- $\mu$ -chloro bridged complexes **2a–2c** were recovered.

These results reveal: (a) that in general, cyclopalladated complexes derived from ferrocenylamines that contain a  $\sigma(\text{Pd}-\text{C}_{\text{sp}^2, \text{ferrocene}})$  bond are less reactive than  $[\{\text{Pd}[(\eta^5\text{-C}_5\text{H}_3\text{CH}_2\text{NMe}_2)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)](\mu\text{-Cl})\}_2]$  **2e**, which undergoes the bis(insertion) of hex-3-yne or diphenylacetylene at room temperature,<sup>8</sup> (b) higher reactivity of the  $\sigma(\text{Pd}-\text{C}_{\text{sp}^2, \text{ferrocene}})$  bond in  $[\{\text{Pd}[(\eta^5\text{-C}_5\text{H}_3\text{C}(\text{Me})=\text{NCH}_2\text{Ph})\text{Fe}(\eta^5\text{-C}_5\text{H}_5)](\mu\text{-Cl})\}_2]$  **2d** when compared with those containing R = H or Ph as substituent on the imine carbon. Consequently, we can conclude that the reactivity of these di- $\mu$ -chloro cyclopalladated derivatives decreases according to the sequence **2e**  $\gg$  **2d** > **2a**, **2b**  $\approx$  **2c**.

As mentioned above the differences observed in the reactivity of cyclopalladated derivatives may be related to a wide variety of factors,<sup>6</sup> including: (a) the lability of the Pd–N bond, (b) the nature of the substituents on the alkyne ligand, (c) the structure and nature of the cyclopalladated ligand, and (d) the remaining ligands bound to the palladium.

Previous studies on compounds of general formulae  $[\{\text{Pd}[(\eta^5\text{-C}_5\text{H}_3\text{CR}=\text{NR}')\text{Fe}(\eta^5\text{-C}_5\text{H}_5)](\mu\text{-Cl})\}_2]$  **2** (R = H, Me or Ph) have demonstrated that the Pd–N bond exhibits high stability, since no evidence of its cleavage was observed even when large excesses of small and basic phosphines (*e.g.*  $\text{PEt}_3$ ) were used.<sup>10,12</sup> In spite of the poor lability of the Pd–N bond in complexes **2a–2d** insertion of the alkyne takes place, which suggests that the reaction is unlikely to have been initiated *via* the cleavage of the Pd–N bond. In order to confirm this hypothesis, we also investigated the reaction of the monomeric compound  $[\text{Pd}\{(\eta^5\text{-C}_5\text{H}_3\text{CH}=\text{NCH}_2\text{Ph})\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}\text{Cl}(\text{PPh}_3)]$  **3a**<sup>10b</sup> with hex-3-yne using identical experimental conditions (hex-3-yne: Pd molar ratio = 2:1, refluxing  $\text{CHCl}_3$  for 1.5 h). In this case most of the starting materials were recovered and no evidence for the formation of either mono- or bis-(insertion) **2a** derivatives was detected by <sup>1</sup>H NMR spectroscopy. Consequently, these results agree with the studies reported recently by Ryabov *et al.*<sup>7</sup> on the insertion of alkynes into the  $\sigma(\text{Pd}-\text{C}_{\text{sp}^2, \text{phenyl}})$  bond of cyclopalladated derivatives containing *N,N*-dimethylbenzylamines  $[\{\text{Pd}(\text{C}_6\text{H}_3\text{RCH}_2\text{NMe}_2)(\mu\text{-X})\}_2]$  (R = H, 4-OMe, 5-Me or 5-F; X = Cl or I) (Fig. 1, A), which contain a more labile Pd–N bond. These authors have shown that the replacement of the di- $\mu$ -chloro-bridged complex by the mononuclear  $[\text{Pd}(\text{C}_6\text{H}_3\text{RCH}_2\text{NMe}_2)\text{X}(\text{py})]$  (py–pyridine) significantly reduces the rate constant, and they have postulated that the first step of the reaction is the opening of the  $\mu\text{-X}$  bridge, followed by the nucleophilic attack of the alkyne.

The two alkynes used in this work hex-3-yne and diphenylacetylene produce the bis(insertion) derivatives (**4a–4d** and **5a–5d**, Scheme 1) in all cases, so the nature of these two substituents does not appear to be especially important in the reactions under study. Since the remaining ligands on the palladium are identical in the four di- $\mu$ -chloro-cyclopalladated derivatives **2a–2d**, the differences observed in the reactivity of complex **2d**, compared with **2a–2c**, should be related to the structure and/or the nature of the chelated ligand.

To our knowledge, no crystal structure of any of these di- $\mu$ -chloro-bridged cyclopalladated complexes **2a–2e** has been reported. However, and as a first approach to rationalizing the differences observed in the reactivity of these compounds (which differ in the chelated ligand), we compared bond lengths and angles in several five-membered cyclopalladated derivatives containing these N-donor ligands derived from ferrocene.<sup>10,12–16</sup> As presented in Table 9, the main differences are found for the Pd–C(6) bond distance which is directly involved in the formation of the C–C bond during the insertion of the former alkyne. Though the minimum values for the Pd–C(6)

bond length correspond to the cyclopalladated complexes containing *N,N*-dimethylferrocenylamine as ligand, for complex **2e** (in which the metallocycle is identical) the insertion of the alkyne is much easier to achieve.<sup>8</sup> In contrast to expectations, the largest Pd–C(6) bond lengths are found for least reactive complexes of general formula  $[\text{Pd}\{(\eta^5\text{-C}_5\text{H}_3\text{CR}=\text{NR}')\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}\text{Cl}(\text{L})]$  (R = H or Ph). Thus the variations observed in the Pd–C(6) bond length do not appear to be responsible for the differences observed in the reactivity of compounds **2a–2e**. However, the Pd–N and/or Pd–Cl bond lengths in the dimeric derivatives might be more important in this respect.

It is well known that in ferrocene derivatives the iron is highly sensitive to minor changes of the substituents of the metallocene, for instance the replacement of the R group on the imine carbon atom is reflected in the Mössbauer parameters as well as in the redox potential of the iron.<sup>10a,11,12,23g,26</sup> Thus a comparative study of the electrochemical behaviour of the iron centre as well as the variations observed in the Mössbauer spectroscopic parameters should be a useful tool to clarify the influence of the nature of the chelated ligands.

Electrochemical cyclic voltammetric studies of compounds **2a–2e** were also undertaken. It is interesting that the di- $\mu$ -chloro derivatives have more cathodic half-wave potentials,  $E_{1/2}$ , than those of the free ligands. According to the general rules established from the electrochemical studies of ferrocene derivatives, the presence of electron-withdrawing substituents inhibits the oxidation of the iron centre, and *vice versa*, electron-donor groups on the ferrocene facilitate oxidation. Taking into account that the uncertainty of the  $E_{1/2}$  measurements is  $\pm 5$  mV, the di- $\mu$ -chloro derivatives can be ordered according to their  $E_{1/2}$  value as follows: **2e**  $\gg$  **2d** > **2a**  $\approx$  **2b**  $\approx$  **2c**.

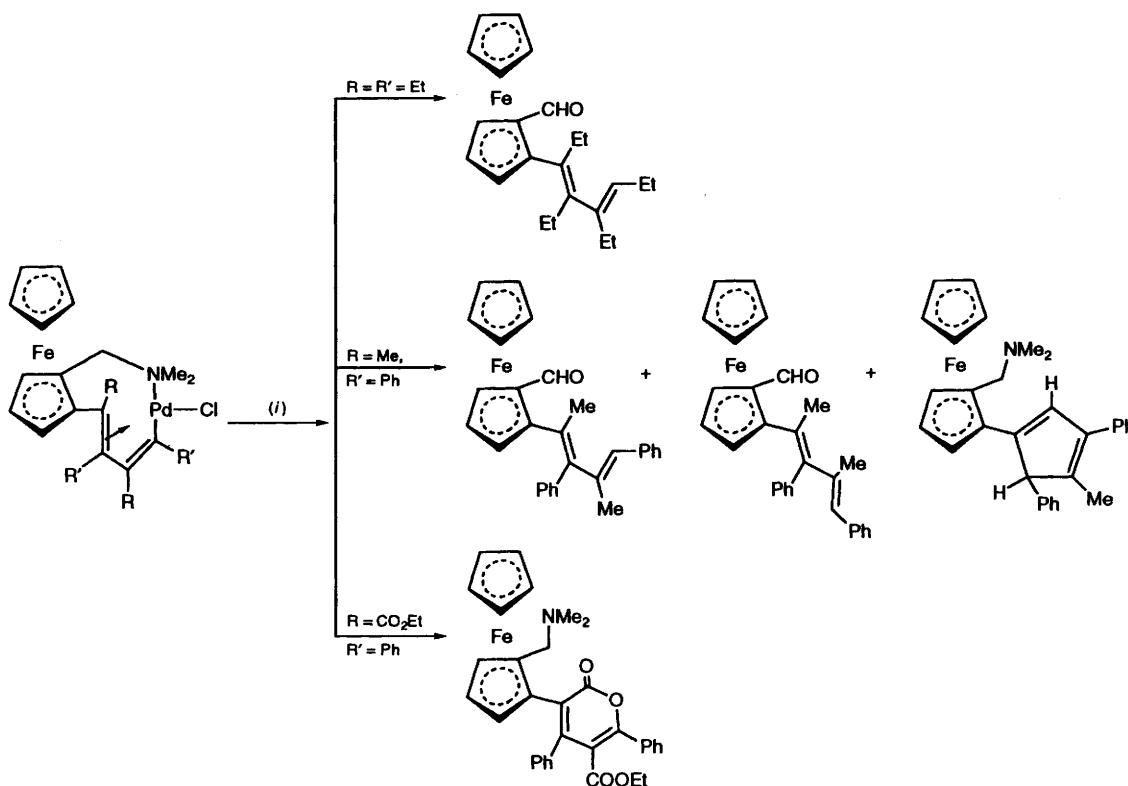
This is consistent with the conclusions reached by Zanello *et al.*<sup>22</sup> on the electrochemical behaviour of penta- and deca-substituted ferrocenes of general formula  $[(\eta^5\text{-C}_5\text{R}_5)\text{Fe}(\eta^5\text{-C}_5\text{R}'_5)]$  (R = H, R' = Me, Et or Ph; R = R' = H, Me or Ph), which show that the substitution of hydrogen atoms of the ferrocene by electron-donor groups (Me or Et)<sup>27</sup> facilitates oxidation of the iron centre.<sup>26</sup>

Although the Mössbauer data for compounds **2a–2e** are not available, we do have data on related unbridged five-membered metallacycles (Table 8). By allowing for the effects of changing ligands on the Mössbauer q.s. values, it can be seen that the resulting q.s. values follow the sequence **2e**  $\gg$  **2d** > **2a**  $\approx$  **2c** > **2b**, an identical sequence to that of the ease of complexes **2a–2e** to undergo alkyne insertions. Consequently, these data allow us to conclude that the electron-donor ability of the chelated ligand enhances the reactivity of the  $\sigma(\text{Pd}-\text{C}_{\text{sp}^2, \text{ferrocene}})$  bond.

**Final Remarks.**—The results reported here show that the di- $\mu$ -chloro-bridged cyclopalladated complexes derived from ferrocenylamines  $[\{\text{Pd}[(\eta^5\text{-C}_5\text{H}_3\text{CR}=\text{NR}')\text{Fe}(\eta^5\text{-C}_5\text{H}_5)](\mu\text{-Cl})\}_2]$  **2a–2d** undergo double insertion of hex-3-yne or diphenylacetylene into the  $\sigma(\text{Pd}-\text{C}_{\text{sp}^2, \text{ferrocene}})$  bond, producing  $[\text{Pd}\{[(\text{R}''\text{C}=\text{CR}')_2(\eta^5\text{-C}_5\text{H}_3\text{CR}=\text{NR}')\text{Fe}(\eta^5\text{-C}_5\text{H}_5)]\}\text{Cl}]$  [R'' = Et (**4a–4d**) or Ph (**5a–5d**)]. Furthermore, the  $\sigma(\text{Pd}-\text{C}_{\text{sp}^2, \text{ferrocene}})$  bond in complexes **2a–2d** is less reactive than in  $[\{\text{Pd}[(\eta^5\text{-C}_5\text{H}_3\text{CH}_2\text{NMe}_2)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)](\mu\text{-Cl})\}_2]$  **2e**. For the dimeric complexes under study (**2a–2d**), the ease with which the bis(insertion) reaction takes place depends on the nature of the substituent at the imine carbon atom (R). An increase in the electron-donor nature of the bidentate ligand facilitates the reaction, consequently, our results support the conclusions reached by Ryabov *et al.*<sup>7</sup> from high-pressure kinetic studies on alkyne insertions into the  $\sigma(\text{Pd}-\text{C}_{\text{sp}^2, \text{phenyl}})$  bond in cyclopalladated derivatives containing *N,N*-dimethylbenzylamines (Fig. 1, A).

In order to clarify the influence of the chelated ligand on cyclopalladated complexes containing a  $\sigma(\text{Pd}-\text{C}_{\text{sp}^2, \text{ferrocene}})$  bond upon the reactivity of these substrates with alkynes,





**Scheme 2** Some examples of the variety of products which can be formed from depalladation reactions of palladium(II) compounds arising from a double insertion of alkynes into  $\sigma(\text{Pd}-\text{C}_{\text{sp}^2, \text{ ferrocene}})$  bonds; (i)  $\text{PPh}_3$ , MeOH, reflux

molecular-orbital calculations on this kind of compounds need to be undertaken. These studies should allow the verification of whether small changes at two (for **2e**), three (for **2a**, **2c** and **2d**) or four (for **2a**, **2b**) bond lengths distance from the  $\sigma(\text{Pd}-\text{C}_{\text{sp}^2, \text{ ferrocene}})$  are important enough as to have a significant effect on the net charge on the metallated carbon atom, which is according to Ryabov *et al.*,<sup>7</sup> the main driving force for the reaction of  $[\{\text{Pd}(\text{C}_6\text{H}_3\text{RCH}_2\text{NMe}_2)(\mu\text{-Cl})\}_2]$  with alkynes.

Depalladation reactions of bis(insertion) products lead to a wide variety of materials the nature of which depends on several factors, especially the nature of the substituents on the butadienyl fragment. Studies in this area have shown that nine-membered palladocycles arising from a double insertion of an alkyne  $\text{RC}\equiv\text{CR}'$  depalladate under mild experimental conditions giving different types of derivatives. These depend on the nature of the R and R' groups,<sup>6,8</sup> as can be easily seen in Scheme 2. Consequently, compounds **4** and **5** appear to be good candidates for elucidating the influence of not only the chelated ligand, but also of the substituents of the inserted alkynes, upon the nature of the final depalladation products. Further reactivity studies in this field are now in progress.

Finally, the results summarized in this paper provide a method of fine tuning the oxidation potentials of the iron(II) {from *ca.*  $-0.20$  to *ca.*  $0.35$  mV} by modifying the nature of the chelate and/or the remaining ligands bound to the palladium.

## Experimental

Elemental analyses (C, H and N) were carried out at the Institut de Química Bio-Orgànica de Barcelona (C.S.I.C.) and at the Servicio de Microanálisis de la Universitat de Barcelona. Infrared spectra were obtained from KBr discs with a Nicolet-520 FTIR spectrophotometer. Proton NMR spectra were recorded at *ca.*  $20^\circ\text{C}$  on Varian-Gemini-200 MHz and Varian VXR-500 MHz instruments using  $\text{CDCl}_3$  (99.8%) and  $\text{SiMe}_4$  as solvent and internal reference respectively. Decomposition

points of the complexes were determined with a Buchi-510 melting point instrument.

**Materials and Syntheses.**—The alkynes (diphenylacetylene and hex-3-yne) were obtained from standard sources and used as received. The di- $\mu$ -chloro-bridged cyclopalladated compounds  $[\{\text{Pd}[(\eta^5\text{-C}_5\text{H}_3\text{CR}=\text{NR}')\text{Fe}(\eta^5\text{-C}_5\text{H}_5)](\mu\text{-Cl})\}_2]$  **2a–2d** and complex **5a** were prepared as described previously.<sup>10,12</sup> All the solvents were dried and distilled before use.

**Preparations.**— $[\text{Pd}\{[(\text{EtC}=\text{CEt})_2(\eta^5\text{-C}_5\text{H}_3\text{CH}=\text{NCH}_2\text{Ph})]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}\text{Cl}]$  **4a**. To a suspension containing 0.250 g (0.28 mmol) of **2a** in chloroform (50  $\text{cm}^3$ ), hex-3-yne (130  $\text{mm}^3$ , 1.14 mmol) was added and the mixture was heated under reflux for 1.5 h. The resulting wine-red solution was concentrated to *ca.* 5  $\text{cm}^3$  on a rotary evaporator, and then passed through a  $\text{SiO}_2$  column (10.0  $\text{mm} \times 250.0$  mm) using  $\text{CHCl}_3$  as eluent. The first fraction was collected and concentrated to dryness on a rotary evaporator. Addition of *n*-hexane to the oily residue produced a precipitate of the compound. Good quality X-ray crystals were grown by slow evaporation of  $\text{CH}_2\text{Cl}_2$ -*n*-hexane (1:1) solutions (yield: 72%) (Found: C, 59.3; H, 5.95; N, 2.30. Calc. for  $\text{C}_{30}\text{H}_{36}\text{ClFeNPd}$ : C, 59.25; H, 5.90; N, 2.30%). IR(KBr pellet),  $\nu(\text{C}=\text{N})$  1605  $\text{cm}^{-1}$ .

$[\text{Pd}\{[(\text{EtC}=\text{CEt})_2(\eta^5\text{-C}_5\text{H}_3\text{CH}=\text{NCH}_2\text{CH}_2\text{Ph})]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}\text{Cl}]$  **4b**. This product was prepared according to the procedure described above for **4a** but using a stoichiometric amount of **2b** as starting material (yield: 79%) (Found: C, 60.0; H, 6.05; N, 2.25. Calc. for  $\text{C}_{31}\text{H}_{38}\text{ClFeNPd}$ : C, 59.85; H, 6.10; N, 2.20%). IR(KBr pellet),  $\nu(\text{C}=\text{N})$  1600  $\text{cm}^{-1}$ .

$[\text{Pd}\{[(\text{PhC}=\text{CPh})_2(\eta^5\text{-C}_5\text{H}_3\text{CH}=\text{NCH}_2\text{CH}_2\text{Ph})]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}\text{Cl}]$  **5b**. The synthesis of this complex was carried out according to the procedure described<sup>12</sup> previously for complex **5a**, but using a stoichiometric amount of **2b** as starting material (yield: 68%) (Found: C, 69.25; H, 4.7; N, 1.75. Calc. for

**Table 10** Crystal data and details of the refinement of the crystal structure of  $[\text{Pd}\{[(\text{EtC}=\text{CEt})_2(\eta^5\text{-C}_5\text{H}_3\text{CR}=\text{NCH}_2\text{Ph})]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}]$  ( $\text{R} = \text{H } \mathbf{4a}$  or  $\text{Me } \mathbf{4d}$ )

	<b>4a</b>	<b>4d</b>
Empirical formula	$\text{C}_{30}\text{H}_{36}\text{ClFeNPd}$	$\text{C}_{31}\text{H}_{38}\text{ClFeNPd}$
<i>M</i>	607.7	622.32
Crystallographic system	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/a$
Crystal size/mm	$0.1 \times 0.1 \times 0.1$	$0.1 \times 0.1 \times 0.1$
<i>T</i> /K	298	293(2)
<i>a</i> /Å	30.783(4)	20.308(4)
<i>b</i> /Å	11.320(2)	11.075(2)
<i>c</i> /Å	20.181(3)	12.565(2)
$\beta$ /°	127.23(3)	92.01(3)
<i>U</i> /Å <sup>3</sup>	5599(3)	2824.3(9)
<i>D<sub>c</sub></i> /g cm <sup>-3</sup>	1.364	1.464
<i>Z</i>	8	4
$\theta$ Range/°	2–30	2.01–25.02
<i>F</i> (000)	2376.0	1280
$\lambda(\text{Mo-K}\alpha)$ /Å	0.710 69	0.710 69
$\mu(\text{Mo-K}\alpha)$ /cm <sup>-1</sup>	11.78	1.264
No. reflections collected	2933	4963
No. of reflections with $I \geq 2\sigma(I)$	2788	4963
No. of parameters	376	287
No. of hydrogens located	19	—
Goodness of fit on $F^2$	—	0.696
$R_1 [I \geq 2.5\sigma(I)]$	0.051	0.041 7
<i>wR</i>	0.055	—
$wR_2 [I \geq 2.5\sigma(I)]$	—	0.096 9
$R_1$ (all data)	—	0.114 4
$wR_2$ (all data)	—	0.238 1
Largest difference peak and hole (e Å <sup>-3</sup> )	—	0.572, -0.895

$\text{C}_{47}\text{H}_{38}\text{ClFeNPd}$ : C, 69.30; H, 4.65; N, 1.70%. IR (KBr pellet),  $\nu(\text{C}=\text{N})$  1602 cm<sup>-1</sup>.

$[\text{Pd}\{[(\text{R}''\text{C}=\text{CR}'')_2(\eta^5\text{-C}_5\text{H}_3\text{CPh}=\text{NCH}_2\text{Ph})]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}]$  ( $\text{R}'' = \text{Et } \mathbf{4c}$  or  $\text{Ph } \mathbf{5c}$ ). Hex-3-yne (50 mm<sup>3</sup>, 0.44 mmol, for **4c**) or diphenylacetylene (80 mg, 0.44 mmol, for **5c**), was slowly added to a suspension containing (0.120 g, 0.110 mmol) **2c** in  $\text{CHCl}_3$  (20 cm<sup>3</sup>). The reaction mixture was refluxed for 1.5 h and then the undissolved materials were removed by filtration and discarded. The deep orange filtrate was concentrated to dryness on a rotary evaporator. The oily residual formed was treated with the minimum amount of  $\text{CHCl}_3$  and then purified by  $\text{SiO}_2$  column (10.0 mm  $\times$  250.0 mm) chromatography using  $\text{CHCl}_3$  as eluent. The reddish fraction was collected and concentrated to dryness on a rotary evaporator. Further treatment of the gummy residual with *n*-hexane, followed by vigorous stirring at room temperature, produced precipitation of the desired complexes. The solid was collected by filtration and air-dried [yields: 72% (**4c**), 75% (**5c**)]. Complex **4c** (Found: C, 63.25; H, 5.9; N, 2.10. Calc. for  $\text{C}_{36}\text{H}_{40}\text{ClFeNPd}$  **4c**: C, 63.20; H, 5.85; N, 2.05%). IR (KBr pellet),  $\nu(\text{C}=\text{N})$  1590 cm<sup>-1</sup>. Complex **5c** (Found: C, 71.3; H, 4.65; N, 1.65. Calc. for  $\text{C}_{52}\text{H}_{40}\text{ClFeNPd}$ : C, 71.20; H, 4.55; N, 1.60%). IR (KBr pellet),  $\nu(\text{C}=\text{N})$  1598 cm<sup>-1</sup>.

$[\text{Pd}\{[(\text{R}''\text{C}=\text{CR}'')_2(\eta^5\text{-C}_5\text{H}_3\text{CMe}=\text{NCH}_2\text{Ph})]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}]$  ( $\text{R}'' = \text{Et } \mathbf{4d}$  or  $\text{Ph } \mathbf{5d}$ ). Complex **2d** (0.200 g, 0.22 mmol) was suspended in chloroform (50 cm<sup>3</sup>) and then the corresponding alkyne (100 mm<sup>3</sup> of hex-3-yne or 0.157 g of diphenylacetylene, 0.88 mmol) was added. The mixture was refluxed for 30 min, and the resulting red solution was concentrated on a rotary evaporator to ca. 5 cm<sup>3</sup>. The oily residue was passed through a  $\text{SiO}_2$  column (10 mm  $\times$  250 mm), using  $\text{CHCl}_3$  as eluent. The orange fraction was collected and concentrated to ca. 5 cm<sup>3</sup> on a rotary evaporator, followed by the addition of *n*-hexane, which produced the precipitation of the complexes. The microcrystalline materials were filtered off

and air-dried (yields: 75 and 79% for **4d** and **5d** respectively). Complex **4d** (Found: C, 59.9; H, 6.15; N, 2.30. Calc. for  $\text{C}_{31}\text{H}_{38}\text{ClFeNPd}$ : C, 59.85; H, 6.10; N, 2.25%). IR (KBr pellet),  $\nu(\text{C}=\text{N})$  1584 cm<sup>-1</sup>. Complex **5d** (Found: C, 69.5; H, 4.7; N, 1.8. Calc. for  $\text{C}_{47}\text{H}_{38}\text{ClFeNPd}$ : C, 69.30; H, 4.65; N, 1.70%). IR (KBr pellet),  $\nu(\text{C}=\text{N})$  1586 cm<sup>-1</sup>.

**Crystal Structure Determination and Refinement.**—Prismatic crystals (sizes in Table 10) of compounds **4a** and **4d** were selected and mounted on an Enraf-Nonius CAD4 (**4a**) or a Philips PW-1100 four-circle diffractometer (**4d**). Unit-cell parameters were determined from automatic centring of 25 reflections (in the ranges shown in Table 10), and refined by least-squares methods using the  $\omega$ -2 $\theta$  scan technique. The number of reflections collected as well as those assumed as observed  $\{I > 2\sigma(I)\}$  are also specified in Table 10. Three reflections were measured every 2 h as orientation and intensity controls and no significant intensity decay was observed. Lorentz polarization corrections were made but not for absorption. The structures were solved by Patterson synthesis, using the SHELXS computer program<sup>28</sup> and refined by full-matrix least-squares methods with the SHELX 76<sup>29</sup> (for **4a**) and with the SHELXL 93<sup>30</sup> (for **4d**) computer programs. The function minimized was  $\sum w|F_o| - |F_c|^2$ , where  $w = \{\sigma^2|F_o| + 0.035|F_o|^2\}^{-1}$  for **4a**, and  $w = \sigma^2(I) + [(0.1063P)^2 + 3.7280P]^{-1}$  [ $P = (|F_o|^2 + 2|F_c|^2)/3$ ] for **4d**;  $f$ ,  $f'$  and  $f''$  values were taken from ref. 31. In complex **4a** one carbon atom of the ethyl group next to the ferrocenyl moiety was located in a disordered position and an occupancy factor of 0.5 was assigned according to the height of the Fourier synthesis peak. For compound **4a**, 19 hydrogen atoms were located from a difference synthesis and 14 were computed, while for **4d**, 33 hydrogen atoms were computed. In both cases, the positions of all hydrogen atoms were refined with an overall isotropic thermal parameter using a riding model for computed hydrogen atoms. Other relevant details concerning the refinement of these crystal structures are summarized in Table 10.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

**Electrochemical Studies.**—Electrochemical data for compounds studied were obtained by cyclic voltametry under  $\text{N}_2$  at 20 °C, using acetonitrile (HPLC grade) as solvent and tetrabutylammonium hexafluorophosphate (0.1 mol dm<sup>-3</sup>) as supporting electrolyte. The redox half-wave potentials  $E_{1/2}$  were referred to an Ag–AgNO<sub>3</sub> (0.1 mol dm<sup>-3</sup> in acetonitrile) electrode separated from the solution by a medium-porosity fritted disc. A platinum wire auxiliary electrode was used in conjunction with a platinum disc working electrode, TACUSSEL-EDI-rotatory electrode (3.14 mm<sup>2</sup>); further details concerning the DACFAMOV apparatus were described previously.<sup>32</sup>

Cyclic voltammograms of ferrocene were recorded before and after each sample to ensure the viability and reproducibility of the results,<sup>33</sup> in particular to test and control the stability of the Ag–AgNO<sub>3</sub> electrode. The cyclic voltammograms of 1 mmol dm<sup>-3</sup> solutions of the samples in acetonitrile were run and the average values of the  $E_{1/2}$  values measured were then referred to ferrocene, which was also used as internal standard to facilitate the interpretation of the results. In all cases the separation between the anodic and cathodic peaks ( $\Delta E = E_{pa} - E_{pc}$ ) and the ratio  $i_{pa}/i_{pc}$  were similar to those obtained for the ferrocene itself under identical experimental conditions. Working under these experimental conditions the standard error of the oxidation potentials is  $\pm 5$  mV.

**Mössbauer Spectra.**—Mössbauer spectra were recorded using solid samples in aluminium holders. The samples were placed in liquid  $\text{N}_2$ , quenched at 78 K and transferred to a cryostat. The spectrometer, previously described,<sup>34</sup> was

calibrated with a 25  $\mu\text{m}$  thick natural iron absorber, which was used as the calibrant (i.s. = 0) for the isomer shift measurements. The spectral data were computer fitted.

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