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Formation of an endo-type nine-membered metallocycle *via* insertion of diphenylacetylene into the σ(Pd-Csp^2, ferrocene) bond. X-Ray crystal structure of $[\overline{\mathrm{Pd}\{\{(C_6H_5\text{–}C{=}C\text{–}C_6H_5)_2(\eta^5\text{-}C_5H_3)\text{–}CH{=}N}\text{–}CH_2\text{–}C_6H_5\}\text{-}Fe(\eta^5\text{-}C_5H_5)\}Cl] \cdot CH_2Cl_2$

Concepción López

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Abstract

Reaction of the di-μ-chloro-bridged cyclopalladated complex $[\{\overline{\mathrm{Pd}[\{(\eta^5\text{-}C_5H_3)\text{–}CH{=}N}\text{–}CH_2\text{–}C_6H_5\}Fe(\eta^5\text{-}C_5H_5)](\mu\text{-}Cl)\}_2]$ (**1**) with diphenylacetylene in a 1:4 molar ratio leads to the formation of the bis(insertion) product, $[\overline{\mathrm{Pd}\{\{(C_6H_5\text{–}C{=}C\text{–}C_6H_5)_2(\eta^5\text{-}C_5H_3)\text{–}CH{=}N}\text{–}CH_2\text{–}C_6H_5\}Fe(\eta^5\text{-}C_5H_5)\}Cl] \cdot CH_2Cl_2$ (**2**). The X-ray crystal structure of this compound is reported. Compound **2** contains a bicyclic system derived from the fusion of the C_5H_3-ring of the ferrocene moiety and an endotype nine-membered metallocycle with two sorts of Pd–C bond. The influences of the σ(Pd–C) bonds and the N-donor upon the ease with which five-membered metallocycles undergo bis(alkyne)insertion reactions are also discussed.

Key words: Palladium; Metallation; Cyclopalladation; X-ray diffraction; Crystal structure

1. Introduction

Cyclometallated compounds, in particular those containing N-donors and palladium, are templates in organometallic and organic syntheses [1–10], for instance carbonylation, vinylation, alkylation and halogenation of this sort of complex have been studied [1] and in most cases this kind of reaction provides alternative pathways for the synthesis of organic compounds. In particular, the study of insertions of symmetric and asymmetric alkynes into the σ(Pd-C) bond has been considerable during the last 5 years [2–10]. Most studies involve the use of five- and six-membered metallocycles containing tertiary amines and σ(Pd–Csp^2, phenyl) or σ(Pd–Csp^3, aliphatic) bonds [2–7,10]. More recently, a few examples of bis(insertions) of alkynes into the σ(Pd–Csp^2, ferrocene) bonds of cyclopalladated complexes containing *N*,*N*′-dimethylaminomethylferrocene have been reported [2,7–9]. Several examples of mono- bis- and even tris-insertions of alkynes have been described [2] which are characterized by the presence of ethylene, butadiene or hexatriene fragments. These compounds are valuable precursors in organic syntheses, since their depalladation usually produces heterocyclic compounds, most of which are close to natural products. To our knowledge none of the studies describes an *N*-donor derived from a ferrocenyl Schiff base or the insertion of alkynes into the σ(Pd–Csp^2, ferrocene) bond.

Schiff bases are interesting and versatile substrates in cyclometallation reactions. Studies on this kind of compound reveal that the two types of five-membered metallocycle can be formed by cyclopalladation (in which the C=N group is either within (endo) or outside

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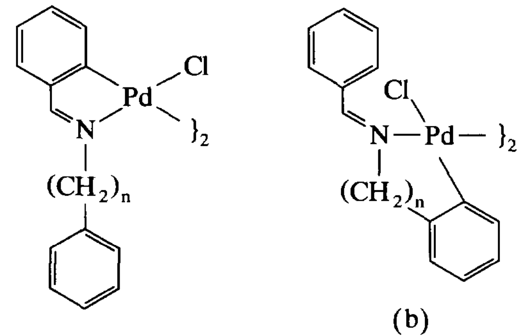


(a) endocyclic structure

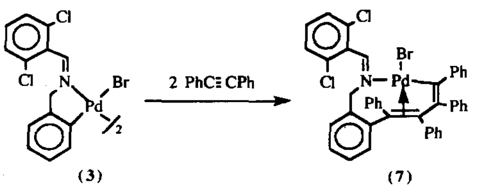
(b) exocyclic structure

Fig. 1. Two types of five-membered metallocycles formed by cyclopalladation. (a) Endocyclic; (b) exocyclic structure.

(exo) the metallacycle, Fig. 1) exhibit different reactivity towards a wide variety of substrates.

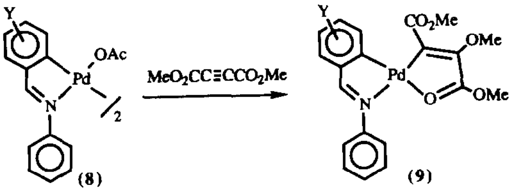
For instance, addition of PPh_2 to exo derivatives such as $[\{\overline{Pd\{C_6H_4-CH_2-N}=CH\text{-}2,6\text{-}(C_6H_3Cl_2)\}(\mu\text{-}Br)\}_2]$ (**3**) cleaves the μ-Br bridges, giving the monomeric compound $[\overline{Pd\{C_6H_4-CH_2-N}=CH\text{-}2,6\text{-}(C_6H_3Cl_2)\}Br(PPh_3)]$ (**4**), but when a large excess of phosphine is used Pd–N bond cleavage also takes place and consequently the metallocycle opens up producing $[Pd\{C_6H_4-CH_2-N=CH\text{-}2,6\text{-}(C_6H_3Cl_2)\}Br(PPh_3)_2]$ (**5**) [11]. However analogous reactions with endo derivatives such as $[\{\overline{Pd(p\text{-}RC_6H_4-CH=N}-C_6H_5)Br\}_2]$ (**6**) have yielded only the monomeric cyclometallated compounds containing a single phosphine per palladium atom [11]. This suggests a higher reactivity of the exotype palladocycles with σ(Pd–Csp^2, phenyl) bonds. These results are also consistent with previous studies on ligand-exchange reactions of cyclopalladated compounds with *N*-donors [12].

Furthermore, the exo complex **3** undergoes double insertion of diphenylacetylene into the σ(Pd–Csp^2, phenyl) bond (eqn. (1)), giving a nine-membered metallocycle (**7**) [10].



(1)

However, attempts to insert more activated acetylenes like $MeO_2CC{\equiv}CCO_2Me$ into the σ(Pd–Csp^2, phenyl) bond of endo cyclopalladated complex **8** (eqn. (2)) were unsuccessful and the reaction produced a complex **9**, which arose from the attack of one of the methoxy groups of the coordinated alkyne [13].



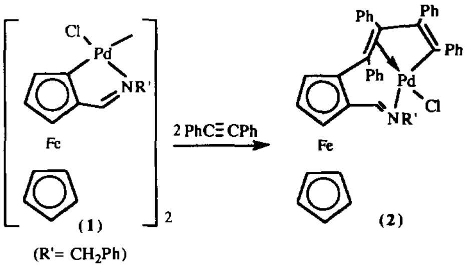
(2)

Only when more reactive cationic endo-type five-membered cyclometallated benzalimines were used as reactants was the monoinsertion of unactivated alkynes observed which allowed Heck *et al.* [4] to synthesize isoquinolium salts.

We have recently reported novel examples of endo-five-membered palladocyclic compounds with σ(Pd–Csp^2, ferrocene) bonds [14]. The reactivity of these systems with phosphines is similar to that above for the endo palladocycles with Schiff bases for which only monophosphine derivatives were obtained [11]. It seemed interesting to compare the reactivity of the two types of Pd–C bond, σ(Pd–Csp^2, phenyl) and σ(Pd–Csp^2, ferrocene) with alkynes. We therefore studied the reaction between diphenylacetylene and the cyclopalladated complex $[\{\overline{Pd[\{(\eta^5\text{-}C_5H_3)-CH=N}-CH_2-C_6H_5\}Fe(\eta^5\text{-}C_5H_5)](\mu\text{-}Cl)\}_2]$ (**1**).

2. Results and discussion

The reaction of **1** and diphenylacetylene in a 1:4 molar ratio was studied under different experimental conditions. Attempts to insert the alkyne under mild conditions (room temperature *ca.* 20°C, using CH_2Cl_2 as solvent and reaction periods from 3 to 24 h) were unsuccessful. The bis(insertion) product **2**, shown in eqn. (3), was only obtained when more drastic experimental conditions were used (in chloroform at reflux).



(3)

Comparison of these results with those reported recently for the insertion of 3-hexyne and diphenylacetylene into the σ(Pd–Csp^2, ferrocene) bond of the cyclopalladated complex $[\{\overline{Pd[\{(\eta^5\text{-}C_5H_3)-CH_2-N}-(CH_3)_2\}Fe(\eta^5\text{-}C_5H_5)](\mu\text{-}Cl)\}_2]$ [2,7–9] shows that alkynes can be inserted more easily into the σ(Pd–C) bond of compounds derived from ferrocenylamines. Since in both cases the metallocycle contains a σ(Pd–Csp^2, ferrocene) bond, the differences observed may be related to other factors such as the steric hindrance arising from the larger bulk of the N–CH_2–C_6H_5 group at the substituent, as well as from the different flexibility of the five-membered metallocycle in the reactants and/or the greater lability of the Pd–N bond in [{Pd[{(η^5-C_5H_3)–CH_2–N–$(CH_3)_2$}Fe(η^5-C_5H_5)](μ-Cl)}$_2$]. In fact, the X-ray crystal structures of the mononuclear derivatives of general formulae: [Pd{{(η^5-C_5H_3)–C(R)=N–$(CH_2)_n$–C_6H_5}Fe(η^5-C_5H_5)}Cl-(PPh_3)] (with R = H or CH_3) and [Pd{{(η^5-C_5H_3)–CH_2–N–$(CH_3)_2$}Fe(η^5-C_5H_5)}Cl(MeIm)] (MeIm = 1-methylimidazole) [14,15] show that while for the Schiff base derivatives the palladium environment is rather crowded and the metallocycle is planar, for their analogue with *N,N*-dimethylaminomethylferrocene the palladocycle has a half-chair conformation.

The new cyclometallated complex is an air-stable orange-red solid, highly soluble in chloroform and dichloromethane, slightly soluble in methanol, ethanol, and ether, and practically insoluble in alkanes and water.

The IR spectrum of complex **2** shows a sharp intense band due to the asymmetric stretching of the C=N bond at 1605 cm^{-1}, which appears at lower wavelengths than in the free base (1612 cm^{-1}) [14]. This fact, which has also been observed for other five-membered cyclopalladated compounds [11,14], was attributed to a decrease in the C=N bond order.

Table 1 shows the principal ^1H NMR chemical shifts of the free base compounds **1** and **2** and related mononuclear cyclopalladated complexes of general formulae [Pd{(η^5-C_5H_5)Fe(η^5-C_5H_3)–CH=N–(CH_2)–C_6H_5}Cl(PR_3)] (R = Ph (**10**), Et (**11**)) and [Pd{(η^5-C_5H_5)Fe(η^5-C_5H_3)–CH=N–(CH_2)–C_6H_5}(dppe)]Cl (**12**) [14].

The imine proton resonance of complexes **1**, **2**, **10** and **12** appears at higher fields than for the free base, indicating that the functional group C=N is contained

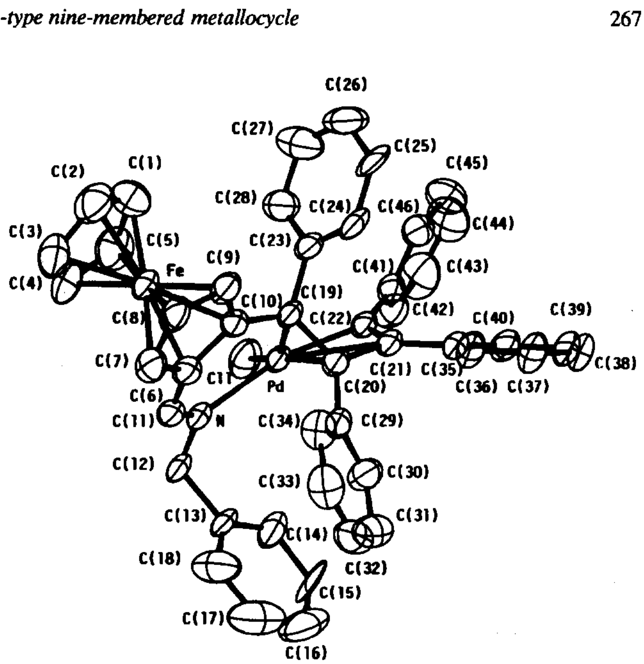
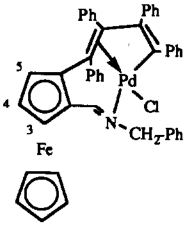


Fig. 2. Molecular structure and atom labelling scheme for compound **2**.

TABLE 1. ^1H NMR spectroscopic data (in ppm) [a] for the free donor, compounds **1** and **2**, and related five-membered metallocycles



	HC=N	H(C_5H_5)	H(5)	H(4)	H(3)	N–CH_2–
[{(η^5-C_5H_3)–CH=N–CH_2–C_6H_5}Fe(η^5-C_5H_5)] [b]	8.24 [c]	4.17	4.68	4.38	4.38	4.68 [c]
[{Pd[{(η^5-C_5H_3)–CH=N–$CH_2C_6H_5$}Fe(η^5-C_5H_5)]Cl}$_2$] [b] (**1**)	7.80 [c]	4.19	4.60	4.31	4.17	4.60 [d] 5.21 [d]
[Pd{{(C_6H_5–C=C–C_6H_5)$_2$(η^5-C_5H_3)–CH=N–CH_2–C_6H_5}Fe(η^5-C_5H_5)}Cl] (**2**)	7.67 [c]	4.15	4.66	4.61	4.37	4.65 [d] 5.45 [d]
[Pd{{(η^5-C_5H_3)–CH=N–CH_2–C_6H_5}Fe(η^5-C_5H_5)}Cl(PPh_3)] (**10**) [b]	7.98 [e]	3.67	4.30	4.00	3.30	4.65 [d] 5.44 [d]
[Pd{{(η^5-C_5H_3)–CH=N–CH_2–C_6H_5}Fe(η^5-C_5H_5)}Cl(PEt_3)] (**11**) [b]	7.95 [e]	4.01	4.37	4.27	4.01	4.60 [d] 5.30 [d]
[Pd{{(η^5-C_5H_3)–CH=N–CH_2–C_6H_5}Fe(η^5-C_5H_5)}(dppe)Cl (**12**) [b]	8.13 [e]	3.93	4.23	3.69	3.93	4.63 [d,f]

[a] Labels refer to the scheme shown above. [b] Data from ref. 14. [c] Singlet. [d] Doublet of doublets (AB pattern) due to the non-equivalence of the two hydrogen atoms. The values given refer to the middle point of each of the two doublets. [e] Doublet due to phosphorus coupling. [f] Overlapped by the resonance of the –CH_2– protons of the dppe.

TABLE 2. Final fractional atomic coordinates [a] for non-hydrogen atoms ($\times 10^4$, except Pd, Fe and Cl, $\times 10^5$) in compound **2**

	x	y	z	B_{eq} [b]
Pd	28178(2)	39505(2)	3190(3)	2.82(1)
Fe	444472(3)	21915(5)	24148(6)	3.46(2)
Cl(1)	32133(7)	42563(11)	−16529(11)	4.93(5)
Cl(2)	64187(13)	90399(23)	31705(21)	9.11(12)
Cl(3)	80786(15)	96472(26)	49511(27)	11.79(14)
N	4022(2)	4873(3)	1446(3)	3.31(13)
C(1)	4734(4)	1797(6)	532(6)	6.02(29)
C(2)	5466(3)	2311(5)	1456(7)	6.44(30)
C(3)	5592(3)	1657(6)	2308(6)	5.98(28)
C(4)	4926(4)	703(5)	1961(7)	6.46(31)
C(5)	4402(4)	791(5)	837(6)	6.04(27)
C(6)	4110(2)	3747(3)	3020(4)	3.42(15)
C(7)	4596(3)	3475(4)	4083(4)	4.17(18)
C(8)	4163(3)	2468(4)	4285(5)	4.38(19)
C(9)	3408(3)	2111(4)	3351(4)	3.76(16)
C(10)	3359(2)	2904(3)	2584(4)	3.17(14)
C(11)	4409(2)	4652(3)	2456(4)	3.46(15)
C(12)	4404(2)	5909(3)	1119(4)	3.87(17)
C(13)	3949(2)	6888(3)	1629(5)	3.90(17)
C(14)	3309(3)	7148(4)	846(5)	4.92(22)
C(15)	2925(4)	8064(6)	1333(9)	7.23(37)
C(16)	3157(6)	8701(5)	2624(11)	8.47(46)
C(17)	3783(6)	8437(6)	3403(9)	8.74(44)
C(18)	4180(4)	7530(5)	2921(6)	6.54(28)
C(19)	2582(2)	2879(3)	1657(3)	2.96(13)
C(20)	2090(2)	3763(3)	1870(4)	3.12(14)
C(21)	1311(2)	3562(3)	849(4)	3.04(14)
C(22)	1582(2)	3396(3)	−330(4)	3.01(13)
C(23)	2156(2)	1693(3)	904(4)	3.64(16)
C(24)	2404(3)	1090(4)	−229(5)	4.64(20)
C(25)	1990(5)	−10(5)	−847(6)	6.44(28)
C(26)	−1340(5)	515(4)	371(8)	7.56(33)
C(27)	1097(4)	69(5)	784(8)	7.01(32)
C(28)	1505(3)	1184(4)	1424(6)	5.15(22)
C(29)	2226(2)	4760(3)	3058(4)	3.31(14)
C(30)	1987(3)	5762(4)	2945(5)	4.38(19)
C(31)	2044(4)	6675(4)	4015(6)	5.41(24)
C(32)	2342(4)	6593(5)	5252(5)	5.53(24)
C(33)	2589(3)	5600(5)	5407(5)	5.48(24)
C(34)	2530(3)	4682(5)	4329(4)	4.58(21)
C(35)	451(2)	3560(3)	1202(4)	3.30(14)
C(36)	−222(3)	3701(4)	335(4)	3.77(17)
C(37)	−1020(3)	3706(4)	683(5)	4.15(19)
C(38)	−1177(3)	3582(4)	1899(6)	4.76(22)
C(39)	−519(3)	3457(5)	2769(5)	4.81(22)
C(40)	289(3)	3447(4)	2434(4)	4.20(18)
C(41)	1111(2)	2924(3)	−1671(4)	3.30(14)
C(42)	611(3)	1847(4)	−1971(5)	4.58(20)
C(43)	135(4)	1386(5)	−3217(6)	6.29(27)
C(44)	143(4)	1973(6)	−4152(6)	4.76(30)
C(45)	654(4)	3021(7)	−3881(6)	6.41(31)
C(46)	1139(3)	3500(4)	−2649(5)	4.41(19)
C(47)	7437(5)	86449(6)	3655(7)	6.74(33)

[a] Standard deviations are given in parentheses.

[b] $B_{eq} = (8\pi^2/3U_{ij}A_i^*A_jA_iA_j)$.

TABLE 3. Bond lengths (in Å) [a] for compound **2**

Cl(1)–Pd	2.353(1)	N–Pd	2.170(3)
C(19)–Pd	2.195(4)	C(20)–Pd	2.162(4)
C(21)–Pd	2.563(4)	C(22)–Pd	2.001(3)
X [b]–Pd	2.059(4)	C(1)–Fe	2.053(6)
C(2)–Fe	2.033(6)	C(3)–Fe	2.047(4)
C(4)–Fe	2.058(7)	C(5)–Fe	2.074(5)
C(6)–Fe	2.036(4)	C(7)–Fe	2.028(4)
C(8)–Fe	2.040(5)	C(9)–Fe	2.042(4)
C(10)–Fe	2.070(4)	C(2)–C(1)	1.410(8)
C(3)–C(2)	1.369(11)	C(4)–C(3)	1.426(8)
C(5)–C(4)	1.417(10)	C(5)–C(1)	1.412(9)
C(7)–C(6)	1.433(6)	C(8)–C(7)	1.418(7)
C(9)–C(8)	1.422(6)	C(10)–C(9)	1.423(6)
C(10)–C(6)	1.435(5)	C(11)–C(6)	1.445(6)
C(11)–N	1.284(6)	C(12)–N	1.480(6)
C(13)–C(12)	1.514(6)	C(14)–C(13)	1.373(7)
C(15)–C(14)	1.378(9)	C(16)–C(15)	1.380(12)
C(17)–C(16)	1.356(14)	C(18)–C(13)	1.382(7)
C(18)–C(17)	1.382(10)	C(19)–C(10)	1.494(5)
C(20)–C(19)	1.422(5)	C(21)–C(20)	1.513(5)
C(22)–C(21)	1.346(5)	C(23)–C(19)	1.512(5)
C(24)–C(23)	1.378(6)	C(25)–C(24)	1.391(6)
C(28)–C(23)	1.386(7)	C(28)–C(27)	1.448(7)
C(29)–C(20)	1.499(5)	C(30)–C(29)	1.372(7)
C(31)–C(30)	1.372(6)	C(32)–C(31)	1.377(8)
C(33)–C(32)	1.380(9)	C(34)–C(29)	1.412(6)
C(34)–C(33)	1.380(7)	C(35)–C(21)	1.474(5)
C(36)–C(35)	1.399(6)	C(40)–C(35)	1.396(7)
C(37)–C(36)	1.378(6)	C(38)–C(37)	1.380(8)
C(39)–C(38)	1.376(7)	C(40)–C(39)	1.387(7)
C(41)–C(22)	1.471(5)	C(42)–C(41)	1.401(6)
C(43)–C(42)	1.393(7)	C(44)–C(43)	1.364(11)
C(45)–C(44)	1.383(10)	C(46)–C(41)	1.396(7)
C(46)–C(45)	1.389(7)	C(47)–Cl(2)	1.739(8)
C(47)–Cl(3)	1.728(7)		

[a] Standard deviations are given in parentheses.

[b] X represents the middle point of the vector defined by the atoms C(19) and C(20).

in the metallocycle. The differences observed for the resonances of the H(5) protons may be attributed to the anisotropy of the phenyl rings of the phosphines (PPh_3 and dppe) and the butadienyl unit in complexes **10**, **12** and **2**, respectively.

The molecular structure of compound **2** and the atom labelling scheme are presented in Fig. 2. Final atomic coordinates for non-hydrogen atoms, as well as bond lengths and angles are given in Tables 2, 3 and 4, respectively.

The structure consists of discrete molecules of $[\overline{\text{Pd}\{(\text{C}_6\text{H}_5\text{–C=C–C}_6\text{H}_5)_2(\eta^5\text{-C}_5\text{H}_3)\text{–CH=N}}\text{–CH}_2\text{–C}_6\text{H}_5\}\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}]$ linked by van der Waals forces, and also contains a CH_2Cl_2 molecule as solvate. The palladium atom is tetracoordinate, bound to a chlorine, Cl(1), the nitrogen, C(22) and the middle-point of the segment defined by the atoms C(19) and C(20) (hereafter referred to as X), in a slightly distorted square-planar environment. The deviations from the mean plane [16*] are as follows: Pd, −0.0072; Cl(1),

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* Reference number with asterisk indicates a note in the list of references.

TABLE 4. Selected bond angles (in degrees) for compound **2** [a]

N–Pd–Cl(1)	92.0(1)	C(19)–Pd–Cl(1)	152.4(1)
C(19)–Pd–N	95.0(1)	C(20)–Pd–Cl(1)	162.5(1)
C(20)–Pd–N	101.5(1)	C(20)–Pd–C(19)	38.1(1)
C(21)–Pd–Cl(1)	127.2(1)	C(21)–Pd–N	134.6(1)
C(21)–Pd–C(19)	61.8(1)	C(21)–Pd–C(20)	36.1(1)
C(22)–Pd–Cl(1)	97.8(1)	C(22)–Pd–N	164.0(1)
C(22)–Pd–C(19)	82.1(1)	C(22)–Pd–C(20)	66.7(1)
C(22)–Pd–C(21)	31.3(1)	C(2)–Fe–C(1)	40.4(2)
C(3)–Fe–C(1)	67.1(3)	C(3)–Fe–C(2)	39.2(3)
C(4)–Fe–C(1)	67.6(3)	C(4)–Fe–C(2)	67.4(3)
C(4)–Fe–C(3)	40.6(2)	C(5)–Fe–C(1)	40.0(3)
C(5)–Fe–C(2)	67.2(2)	C(5)–Fe–C(3)	67.2(2)
C(5)–Fe–C(4)	40.1(3)	C(6)–Fe–C(1)	114.8(2)
C(6)–Fe–C(2)	109.7(2)	C(6)–Fe–C(3)	133.1(2)
C(6)–Fe–C(4)	172.9(2)	C(6)–Fe–C(5)	145.8(2)
C(7)–Fe–C(1)	142.7(2)	C(7)–Fe–C(2)	111.2(2)
C(7)–Fe–C(3)	106.9(2)	C(7)–Fe–C(4)	132.8(2)
C(7)–Fe–C(5)	172.9(2)	C(7)–Fe–C(6)	41.3(2)
C(8)–Fe–C(1)	176.0(2)	C(8)–Fe–C(2)	140.2(2)
C(8)–Fe–C(3)	111.1(2)	C(8)–Fe–C(4)	108.6(3)
C(8)–Fe–C(5)	136.2(2)	C(8)–Fe–C(6)	69.2(2)
C(8)–Fe–C(7)	40.8(2)	C(9)–Fe–C(1)	138.9(2)
C(9)–Fe–C(2)	178.1(2)	C(9)–Fe–C(3)	142.7(2)
C(9)–Fe–C(4)	114.2(2)	C(9)–Fe–C(5)	113.3(2)
C(9)–Fe–C(6)	68.8(2)	C(9)–Fe–C(7)	68.6(2)
C(9)–Fe–C(8)	40.8(2)	C(11)–N–Pd	125.4(3)
C(12)–N–Pd	118.3(2)	C(12)–N–C(11)	116.0(3)
C(3)–C(2)–C(1)	109.2(6)	C(4)–C(3)–C(2)	108.6(5)
C(5)–C(4)–C(3)	106.8(6)	C(4)–C(5)–C(1)	108.0(5)
C(8)–C(7)–C(6)	108.5(3)	C(9)–C(8)–C(7)	107.7(4)
C(10)–C(6)–C(7)	107.5(4)	C(10)–C(9)–C(8)	108.9(4)
C(11)–C(6)–C(10)	128.9(4)	C(19)–C(10)–C(6)	129.6(4)
C(19)–C(10)–C(9)	122.5(3)	C(6)–C(11)–N	125.3(3)
C(13)–C(12)–N	110.9(3)	C(14)–C(13)–C(12)	121.8(4)
C(18)–C(13)–C(12)	119.1(4)	C(18)–C(13)–C(14)	119.1(5)
C(15)–C(14)–C(13)	120.2(5)	C(16)–C(15)–C(14)	120.5(7)
C(17)–C(16)–C(15)	119.4(7)	C(18)–C(17)–C(16)	120.7(7)
C(18)–C(18)–C(13)	120.1(6)	C(10)–C(19)–Pd	112.5(2)
C(20)–C(19)–Pd	69.7(2)	C(20)–C(19)–C(10)	121.1(3)
C(23)–C(19)–Pd	111.2(3)	C(23)–C(19)–C(10)	113.2(3)
C(23)–C(19)–C(20)	119.2(3)	C(19)–C(20)–Pd	72.2(2)
C(21)–C(20)–Pd	86.6(2)	C(21)–C(20)–C(19)	114.1(3)
C(29)–C(20)–Pd	116.1(3)	C(29)–C(20)–C(19)	126.0(3)
C(29)–C(20)–C(21)	119.5(3)	C(20)–C(21)–Pd	57.3(2)
C(22)–C(21)–Pd	50.6(2)	C(22)–C(21)–C(20)	106.5(3)
C(35)–C(21)–Pd	169.7(3)	C(35)–C(21)–C(20)	122.5(3)
C(35)–C(21)–C(22)	131.0(3)	C(21)–C(22)–Pd	98.0(2)
C(41)–C(22)–Pd	131.4(3)	C(41)–C(22)–C(21)	130.5(3)
C(24)–C(23)–C(19)	123.4(4)	C(28)–C(23)–C(19)	117.3(4)
C(28)–C(23)–C(24)	119.3(4)	C(25)–C(24)–C(23)	119.8(5)
C(27)–C(28)–C(23)	120.0(5)	C(30)–C(29)–C(20)	119.9(4)
C(34)–C(29)–C(20)	122.0(4)	C(34)–C(29)–C(30)	117.8(4)
C(31)–C(30)–C(29)	122.3(5)	C(32)–C(31)–C(30)	119.5(5)
C(33)–C(32)–C(31)	120.0(5)	C(34)–C(33)–C(32)	120.4(5)
C(33)–C(34)–C(29)	120.0(5)	C(36)–C(35)–C(21)	121.5(4)
C(40)–C(35)–C(21)	120.7(4)	C(40)–C(35)–C(36)	117.8(4)
C(37)–C(36)–C(35)	120.7(4)	C(38)–C(37)–C(36)	121.1(4)
C(39)–C(38)–C(37)	118.8(5)	C(40)–C(39)–C(38)	120.9(5)
C(39)–C(40)–C(35)	120.6(4)	C(42)–C(41)–C(22)	118.1(4)
C(42)–C(41)–C(22)	118.1(4)	C(46)–C(41)–C(42)	118.9(4)
C(43)–C(42)–C(41)	119.8(5)	C(44)–C(43)–C(42)	120.8(5)
C(45)–C(44)–C(43)	119.9(5)	C(46)–C(45)–C(44)	120.5(7)
C(45)–C(46)–C(44)	120.5(7)	Cl(3)–C(47)–Cl(2)	113.8(4)

[a] Standard deviations are given in parentheses.

−0.1884; N, +0.2077; C(22), +0.2585; and X, −0.2705. The Pd–N, Pd–Cl(1), and Pd–C(22) bond lengths are similar to those found in five-membered cyclopalladated compounds [17]. The Pd–C(19) and Pd–C(20) lengths [2.195(4) and 2.162(4) Å, respectively] are slightly different from one another, and the angle C(19)–Pd–C(20) is 38.(1)°. The C(19)–C(20) double bond forms a dihedral angle of 75.4° with the coordination plane of the complex. On the other hand, the C(21)–C(22) bond is clearly shorter than the C(19)–C(20) double bond, and these differences can be attributed to the different type of coordination of the two groups to the palladium atom (η^1- and η^2-, respectively).

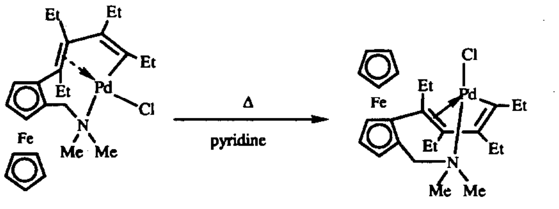
The complex contains a bicyclic system which is formed by the fusion of the substituted pentagonal ring of the ferrocene-moiety and a nine-membered metallocycle. The orientation of the inserted butadienyl fragment with respect to the ferrocenylimine fragment is defined by the angle of 44.5° between the two planes formed by the sets of atoms: [C(6), C(10), C(11), N and Pd] and [C(19), C(20), C(21) and C(22)]. Notice also that the former set of atoms is not precisely coplanar {max. deviation = 0.010 Å for C(10)}, and the latter set forms a very flat pyramid.

The C=N functional group is contained in the nine-membered metallocycle, thus confirming its endo structure. The C=N bond length [1.284(3) Å] is similar to that reported for related five-membered metallocycles $[\overline{\mathrm{Pd}\{\{(\eta^5\text{-}C_5H_3)\text{-}C(R)=\mathrm{N}}\text{-}(CH_2)_n\text{-}C_6H_5\}Fe(\eta^5\text{-}C_5H_5)\}Cl(PR'_3)]$ [14,15], and clearly larger than those found in related ferrocenylimines (*ca.* 1.24–1.26 Å) [15]. The imine ligand has an *anti*-conformation as reflected by the torsion angle C(6)–C(11)–N–C(12) [−178.18°] and the orientation of the phenyl ring on the imine substituent is almost perpendicular (109.71°) to the 1,2-disubstituted C_5H_3 ring of the ferrocene moiety. The distance between the two metal atoms [4.378 Å] is shorter than that found by Pfeffer and Heck *et al.* [7,8] for the two isomers of $[\overline{\mathrm{Pd}\{\{(EtC=CEt)_2(\eta^5\text{-}C_5H_3)\text{-}CH_2\text{-}\mathrm{N}}(CH_3)_2\}Fe(\eta^5\text{-}C_5H_5)\}Cl]$ (**14**, **15**), but it is clearly longer than that found [3.58–3.59 Å] for cyclopalladated complexes containing σ(Pd–Csp^2, ferrocene) bonds [17], and consequently, there is no direct interaction between Pd and Fe.

The average C–C bond length in the two pentagonal rings [1.416(7)°] is similar to the values reported for other ferrocene derivatives [17]. The Fe–C (ring) bond distance ranges from 2.028(4) to 2.074(5) Å. The two pentagonal rings are parallel (tilt angle 4.90°) and nearly staggered as reflected in the twist angle [18] (average value 24.5°).

The phenyl substituents on the double bond C(19)–C(20) are *trans* to each other, and those of the C(21)–C(22) are *cis*. This arrangement provides less steric hindrance between the remaining substituents.

The X-ray crystal structure of **2** (Fig. 2) shows that the C(19)–C(20) bond of the butadienyl unit is located above the plane defined by the atoms N, C(11) and C(6) opposite the iron centre and the C_5H_5-moiety of the ferrocene group; and the phenyl substituent at the C(19) carbon atom is oriented towards the unsubstituted pentagonal ring [C(1)–C(5)]. This orientation is similar to that reported for $[Pd\{\{(RC{=}CR)_2(\eta^5\text{-}C_5H_3)\text{-}CH_2\text{-}N(CH_3)_2\}Fe(\eta^5\text{-}C_5H_5)\}Cl]$ compounds [7,8a,b], with R = Ph (**13**) or Et (**14**). Complex **14** undergoes isomerization when heated under reflux in pyridine for 1.5 h giving its diastereoisomer **15** (eqn. (4)). This has been interpreted in terms of an inversion of either the ferrocene moiety, or the nine-membered palladocyclic ring. Moreover, Pfeffer *et al.* [8] have attributed the driving force for such a change in configuration to steric effects arising from the different orientations of the ethyl groups closer to the ferrocene moiety.



(**14**) (**15**) (4)

Although the insertion reaction was carried out at higher temperature in our case, no evidence of the formation of any other isomer of complex **2** was detected. This may be then attributed to the different "effective bulk" of the substituents at the carbon atom of the η^2-butadienyl moiety, phenyl and ethyl. When the insertion of diphenylacetylene into the σ(Pd–Csp^2, ferrocene) bond of $[\{Pd[\{(\eta^5\text{-}C_5H_3)\text{-}CH_2N\text{-}(CH_3)_2\}Fe(\eta^5\text{-}C_5H_5)](\mu\text{-}Cl)\}_2]$ was carried out at higher temperatures, depalladation occurred and the formation of six- and seven-membered rings took place *via* annulation reactions.

There are no significant differences between bond lengths or angles of the nine-membered metallocycle in complex **2** and those reported previously for analogous derivatives obtained from bis(insertion) reactions of acetylenes into different types of palladocycles containing σ(Pd-Csp^2, phenyl) or σ(Pd-Csp^2, ferrocene) bonds [17].

The results reported here are in contrast with those described recently for alkyne insertions into the σ(Pd–C) bonds of cyclopalladated compounds containing *N*,*N*-dimethylaminobenzene and *N*,*N*-dimethylaminomethylferrocene. The two sorts of metal–carbon bond (Pd–Csp^2, phenyl) and (Pd–Csp^2, ferrocene) show similar reactivity towards alkynes, and the bis(insertion) products were obtained in both cases. However, when cyclometallated complexes containing Schiff bases are used as substrates in these reactions, the results differ significantly. The endo five-membered palladocycles with a σ(Pd–Csp^2, ferrocene) bond appear to be more reactive than their analogues derived from organic imines which contain σ(Pd–Csp^2, phenyl) bonds. For the endo systems under study, the bis(insertion) of diphenylacetylene is achieved quite easily, producing a nine-membered ring which contains the fuctional group C=N, while for their analogues containing Schiff bases no similar reaction has yet been reported. Only when very reactive cationic cyclopalladated benzalimines were used, was the insertion of alkynes achieved, and isoquinolinium salts produced [4]. From this point of view, five-membered metallocycles derived from ferrocenylimines are similar to the more reactive exo palladocycles with σ(Pd–Csp^2, phenyl) bonds, which also incorporate a four carbon unit (two alkyne molecules) into the σ(Pd–C) bond when the reaction is carried out in chloroform under reflux for 18 h [10]. Consequently, as a first approach, the ease with which five-membered metallocycles containing σ(Pd–Csp^2) bonds undergo alkyne insertions can be summarized, as follows:

Organic imine < Organic imine < Ferrocenylimine
(endo) (exo) (endo)
< Ferrocenylamine

Furthermore, as is well known [2], the reactions of cyclopalladated compounds and alkynes followed by depalladation processes lead to a wide variety of products, the nature of which is clearly dependent on several factors. Recent studies on [2,8c,9] have shown that the nature of the substituents of the butadienyl fragment modifies the final products of these reactions. Other factors such as the cyclometallated ligand, the stoichiometry and the remaining ligands coordinated to the palladium are also important. Consequently, complex **2** appears to be a good substrate for clarifying the influence of the cyclopalladated ligand upon final depalladation products, in particular by comparing them with those reported by Pfeffer *et al.* [2,8,9]. Reactivity studies on complex **2** need to be undertaken to elucidate the role of the cyclopalladated ligand (ferrocenylamines *versus* ferrocenylimines) in these reactions. Moreover, the presence of a functional group inside the nine-membered metallocycle may open alternative pathways for the syntheses of difunctionalized 1,2-disubstituted ferrocene derivatives.

3. Experimental details

Elemental analyses (C, H and N) were carried out at the Institut de Química Bio-Orgânica de Barcelona (C.S.I.C.). Infrared spectra were obtained from KBr disks with a Perkin-Elmer 1330-spectrophotometer. ^{1}H-NMR-spectrum was recorded at *ca.* 20°C on a Varian-VXR-500MHz instrument, using $CDCl_3$ (99.8%) and $Si(CH_3)_4$ as solvent and internal reference, respectively.

3.1. Syntheses of the compounds

The ferrocenylimine $[(\eta^5\text{-}C_5H_4)\text{–}CH\text{=}N\text{–}CH_2\text{–}C_6H_5)Fe(\eta^5\text{-}C_5H_5)]$ and the di-μ-chloro-bridged complex **1** were prepared as described previously [14]. Diphenylacetylene was obtained from standard sources and used as received. The solvents were dried and distilled before use.

Preparation of complex $[Pd\{(C_6H_5\text{–}C\text{=}C\text{–}C_6H_5)_2\text{-}(\eta^5\text{-}C_5H_3)\text{–}CH\text{=}N\text{–}CH_2\text{–}C_6H_5\}Fe(\eta^5\text{-}C_5H_5)Cl]\cdot CH_2Cl_2$ *(**2**)*. To a mixture containing 0.50 g (0.56 mmol) of $[\{Pd[(\eta^5\text{-}C_5H_3)\text{–}CH\text{=}N\text{–}CH_2\text{–}C_6H_5\}Fe((\eta^5\text{-}C_5H_5)]\text{-}(\mu\text{-}Cl)\}_2]$ (**1**), in 50 ml of chloroform, 0.40 g (2.24 mmol) of diphenylacetylene was added, and the resulting mixture was heated under reflux for 1.5 h. When the mixture had cooled to *ca.* 20°C, the undissolved materials were removed by filtration and the wine-red filtrate was concentrated to dryness on a rotary evaporator. The oil formed was treated with 30 ml of hexane and stirred at room temperature for 30 min. The precipitate was collected by filtration and air-dried. The product was purified by SiO_2-column chromatography (10.0 mm × 250.0 mm); using $CHCl_3$ as eluant. The red fraction was collected and concentrated to *ca.* 5 ml on a rotary evaporator. Addition of hexane (20 ml) precipitated the complex, which was collected by filtration and air-dried. Good quality crystals of compound **2** were obtained by slow evaporation of concentrated CH_2Cl_2: hexane (1:2) solutions of the complex at *ca.* 4°C. Yield: 66.2%.

Anal. Found: C, 61.15; H, 4.72; N, 1.75. $C_{42}H_{38}Cl_3FeNPd$ calcd.: C, 61.08; H, 4.64; N, 1.70%. IR (KBr, disks) ν(C=N): 1605 cm^{-1}. m.p 185–189°C (decomp).

3.2. Crystal data for compound 2

$C_{41}H_{36}ClFeNPd \cdot CH_2Cl_2$. FW = 885.44, triclinic, $a = 16.114(3)$, $b = 12.352(2)$, $c = 10.594(2)$ Å, $\alpha = 104.32(2)$, $\beta = 96.42(3)$ and $\gamma = 97.73(3)°$, space group $P1$, $V = 2001(1)$ Å^3, $D_x = 1.469$ g cm^{-3}, $Z = 2$; $F(000) = 900.0$, λ(Mo $K\alpha$) = 0.71069 Å, μ(Mo $K\alpha$) = 10.46 cm^{-1}.

3.3. Crystal structure determination and refinement

A prismatic crystal ($0.1 \times 0.1 \times 0.2$ mm^3) of compound **2** was selected and mounted on a Phillips PW-1100 difractometer. Unit cell parameters were determined from automatic centring of 25 reflections ($8° \le \Theta \le 16°$) and refined by a least-squares method. Intensities were collected with a graphite monochromatized Mo Kα radiation using the ω–2Θ scan technique. A total of 7480 reflections were measured in the range $2° \le \Theta \le 30°$, and 7341 were assumed as observed applying the condition $I > 2.5\sigma(I)$. Three reflections were measured every 2 h as orientation and intensity control and no significant intensity decay was observed. Lorentz polarization corrections were made, but absorption corrections were not.

The structure was solved by Patterson synthesis, using the SHELXS computer program [19], and refined by full-matrix least-squares method with the SHELX76 computer program [20]. The function minimized was: $\Sigma w(|F_o|^2 - |F_c|)^2$, where $w = \{\sigma^2(F_o) + 0.008|F_o|^2\}^{-1}$, f, f' and f'' were taken from *International Tables of X-Ray Crystallography* [21]. The position of one hydrogen atom was computed and the remainder were located from a difference synthesis. All were refined with an overall isotropic temperature factor using a riding model for computed H-atoms. The final R factor was 0.047 ($R_w = 0.054$). The number of parameters refined was 592. Max. shifts/e.s.d. = 0.06. Maximum and minimum peaks in the final difference syntheses were 0.4 and −0.3 e Å^{-3}, respectively.

Supplementary material. Tables containing final atomic coordinates for all the atoms, a complete list of bond lengths and angles, anisotropic thermal parameters, and bond lengths and angles involving hydrogen atoms for complex **2** have been deposited at the Cambridge Crystallographic Data Centre, and these plus structure factor tables, are also available from the authors upon request.

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