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Comparative Study of the Reactivity of Cyclopalladated Compounds Containing [C(sp^2,ferrocene),N,N′]$^-$ Terdentate Ligands versus Symmetric Alkynes

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A comparative study of the reactivity of the cyclopalladated compounds [Pd{[(η^5-C_5H_3)-CH=N(CH_2)$_n$NMe_2]Fe(η^5-C_5H_5)}Cl] (n = 2 (**2a**), 3 (**2b**)) containing a [C(sp^2,ferrocene),N,N′]$^-$ terdentate group with the symmetric alkynes $R^1C{\equiv}CR^1$ (with R^1 = Ph, Et, CO_2Me) is reported. In the presence of Tl[BF_4], these reactions have allowed us to isolate and characterize ionic palladacycles of the general formula [Pd{[($R^1C{=}CR^1$)$_2$(η^5-C_5H_3)CH=N(CH_2)$_n$NMe_2]Fe(η^5-C_5H_5)}][BF_4] (n = 2, R^1 = Ph (**4a**), Et (**5a**), CO_2Me (**6a**); n = 3, R^1 = Ph (**4b**), Et (**5b**), CO_2Me (**6b**)) and the neutral derivatives [Pd{[($MeO_2CC{=}CCO_2Me$)(η^5-C_5H_3)-CH=N(CH_2)$_n$NMe_2]Fe(η^5-C_5H_5)}Cl] (n = 2 (**7a**), 3 (**7b**)) and [Pd{[($MeO_2CC{=}CCO_2Me$)$_2$(η^5-C_5H_3)CH=N(CH_2)$_3$NMe_2]Fe(η^5-C_5H_5)}Cl] (**8b**). Compounds **4**−**6** and **8b** arise from the bis insertion of the corresponding alkynes into the σ[Pd−C(sp^2,ferrocene)] bond of **2**, while the formation of **7** involved the insertion of only one molecule of $MeO_2CC{\equiv}CCO_2Me$. The mode of binding of the butadienyl unit is η^3 in **4**−**6** and η^1 in **8b**. Compounds **7** could also be isolated in a higher yield from the reaction of equimolar amounts of $MeO_2CC{\equiv}CCO_2Me$ and the corresponding compound **2** in refluxing CH_2Cl_2. The X-ray crystal structures of **4a**,**b**, **5b**, and **8b** are also reported and confirm the mode of binding of the ferrocenyl ligand to the palladium in these compounds.

Introduction

The synthesis, characterization, and study of cyclopalladated complexes[1] has attracted great interest during the past decade due to a variety of interesting applications in different areas.[2−11] Some examples of metallomesogens or antitumor drugs containing palladacycles have been reported,[3,4] and the applications of chiral cyclopalladated complexes for the determination of enantiomeric excesses of chiral reagents have also been described.[5] More recently, some articles focused on the catalytic activities of these sorts of compounds have also been reported.[6] However, one of the main interests of cyclopalladated derivatives is based on their use either as building blocks for the preparation of macromolecules[7] or as precursors for organic or organometallic synthesis.[8,9] For instance, cyclopalladated compounds show high reactivity toward a wide variety of substrates such as CO, isonitriles, alkenes, and alkynes. Reactions of this kind have provided novel procedures for the preparation of organic compounds.[8] Mono, bis, and even tris insertions of alkynes into the

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Chart 1

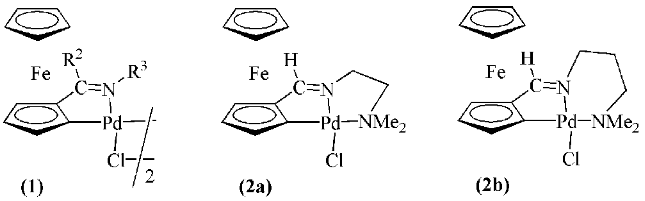


Table 1. Electronic and Steric Parameters for the Substituents (R^1) on the Alkynes[a]

R^1	σ_I	σ_R	Es′(CH)
Ph	0.12	0.10	3.0
Et	−0.01	−0.14	2.0
CO_2Me	0.21	0.16	4.0

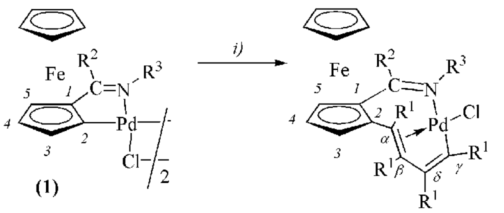
[a] σ_I and σ_R are the inductive (para) and mesomeric (para) parameters of the substituent R^1. Positive σ values indicate electron-withdrawing character of the substituent, while negative values correspond to electron-donor groups. Es′(CH) values are Charton's steric parameters for R^1 calculated according to structural data. All the values presented in this table were taken from ref 15.

σ[Pd−C(sp^2,aryl)] bond of cyclopalladated complexes containing organic ligands have been extensively studied over the last few years,[8−10] and a few examples of the mono and bis insertion of internal alkynes into the σ[Pd−C(sp^2,ferrocene)] bond of the bis(μ-chloro) cyclopalladated compounds [Pd{[(η^5-C_5H_3)C(R^2)=NR^3]Fe(η^5-C_5H_5)}(μ-Cl)]$_2$ (**1**) (Chart 1) containing bidentate [C(sp^2,ferrocene),N]$^-$ ferrocenyl Schiff bases have also been reported.[10−12]

Cyclopalladated complexes with a [C(sp^2,ferrocene),N,N′]$^-$ terdentate ligand are scarce,[13,14] and to the best of our knowledge, the reactivity of the σ[Pd−C(sp^2,ferrocene)] bond with alkynes in these types of compounds has not been studied so far.

In view of these facts, we were prompted to study the reactions of compounds [Pd{[(η^5-C_5H_3)CH=N$(CH_2)_n$NMe$_2$]Fe(η^5-C_5H_5)}Cl] (n = 2 (**2a**), 3 (**2b**)) (Chart 1) with three different internal alkynes $R^1C{\equiv}CR^1$ (where R^1 represents Et, Ph, or CO_2Me), which differ in the electronic and steric properties of the substituents R^1 (Table 1).[15] This type of study could be useful to elucidate the relative influence of: (a) the mode of binding of the ferrocenyl ligand, [C(sp^2,ferrocene),N]$^-$ in **1** or [C(sp^2,ferrocene),N,N′]$^-$ in **2**, (b) the substituents on the alkyne (electron-donating/electron-withdrawing character as well as their bulk), (c) the type of σ(Pd−Cl) bond in **1** or **2**, and even (d) the relevancy of the size of the chelate formed by the binding of the two nitrogen atoms to the palladium, a five- (in **2a**) or a six-membered ring (in **2b**), upon the nature of the final product.

Scheme 1[a]



[a] Abbreviations: R^2 = H, Me, Ph; R^3 = phenyl, benzyl, 2,2′-biphenyl; R^1 = Ph, Et. Legend: (i) diphenylacetylene or hex-3-yne in a alkyne/Pd molar ratio of 2, in refluxing CH_2Cl_2 or $CHCl_3$ for 2 h, followed by SiO_2 column chromatography.

Results and Discussion

Alkyne Insertions. In a first attempt to study the reactivity of compounds **2** with the alkynes, we decided to use the procedures described previously for the preparation of [Pd{[($R^1C{=}CR^1$)$_2$(η^5-C_5H_3)C(R^2)=NR^3]Fe(η^5-C_5H_5)}Cl] (R^1 = Et, Ph; R^2 = H, Me, Ph; R^3 = phenyl, benzyl groups),[12] which consisted of the reaction of the corresponding bis(μ-chloro) cyclopalladated derivative [Pd{[(η^5-C_5H_3)C(R^2)=NR^3]Fe(η^5-C_5H_5)}(μ-Cl)]$_2$ (**1**) with PhC≡CPh or EtC≡CEt (Pd/alkyne molar ratio of 2) in refluxing CH_2Cl_2 for 2 h (Scheme 1).[12]

However, when [Pd{[(η^5-C_5H_3)CH=N$(CH_2)_n$NMe$_2$]Fe(η^5-C_5H_5)}Cl] (n = 2 (**2a**), 3 (**2b**)) (Chart 1) was treated separately with PhC≡CPh or EtC≡CEt (alkyne/Pd molar ratio of 2) in refluxing CH_2Cl_2 (or $CHCl_3$) for 2 h, the starting materials were recovered unchanged and no evidence of any chemical change was detected by NMR spectroscopy, even when the refluxing period was increased up to 24 h. These results are in sharp contrast with those reported previously for the dimeric compounds [Pd{[(η^5-C_5H_3)C(R^2)=NR^3]Fe(η^5-C_5H_5)}(μ-Cl)]$_2$ (**1**),[12] thus suggesting that the bis(μ-chloro) cyclopalladated complexes are more prone to undergo the double insertion of the alkynes $R^1C{\equiv}CR^1$ (with R^1 = Ph, Et) than compounds **2**.

According to the mechanistic studies reported by Ryabov et al.[16] on the bis(insertion) of alkynes into the σ[Pd−C(sp^2,aryl)] bond of cyclopalladated complexes, in these kinds of reactions, the first step of the process consists of the coordination of the alkyne to the Pd(II) in a cis arrangement to metalated carbon. The smaller proclivity of **2a**,**b** to react with diphenylacetylene or hex-3-yne, when compared with that of compounds **1**, could be related to the different lability of the Pd−Cl bond in the adjacent position to the metalated carbon.

To check this hypothesis, we decided to elucidate if the removal of the chlorine group in **2**, upon the addition of thallium(I) salts, could enhance the reactivity of these substrates with PhC≡CPh or EtC≡CEt. With this aim, and as a first approach to the problem, **2a** was treated separately in acetone with a 50% excess of Tl[BF$_4$] at room temperature (ca. 20 °C) for 2 h. During this period, the precipitation of TlCl was observed. The subsequent removal of the TlCl (~26 mg) and the excess of Tl[BF$_4$] and the concentration of the resulting solution to dryness on a rotary evaporator gave a red-brown residue (hereinafter referred to as **3a**). This material was then treated separately with diphenylacetylene in a alkyne/

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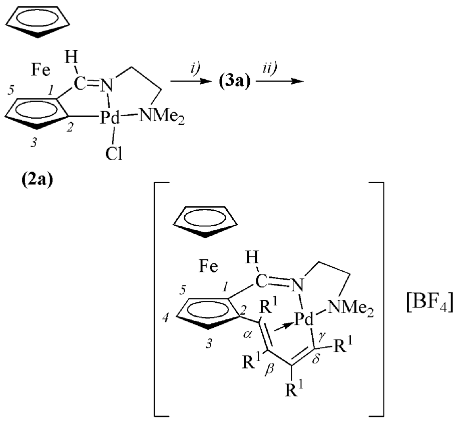
Scheme 2[a]



(2a)

R^1 = Ph (4a) or Et (5a)

[a] Legend: (i) Tl[BF$_4$] in acetone (molar ratio Tl(I)/**2a** = 1.5) at room temperature, followed by the removal of the TlCl by filtration and the unreacted Tl[BF$_4$] using CH$_2$Cl$_2$ and subsequent evaporation to dryness; (ii) The corresponding alkyne diphenylacetylene or hex-3-yne in a alkyne/Pd molar ratio of 2, in refluxing CH$_2$Cl$_2$, followed by SiO$_2$ column chromatography (see text).

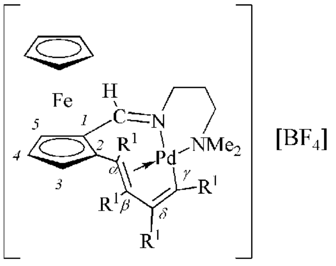
palladium(II) molar ratio of 2, in refluxing CH$_2$Cl$_2$ for 2 h (Scheme 2). Two different compounds (red and orange-brown solids) were isolated after workup by short SiO$_2$ column chromatography. The red solid was obtained from the band eluted with CH$_2$Cl$_2$, and its characterization data were identical with those of the starting material [Pd{[(η^5-C$_5$H$_3$)-CH=N(CH$_2$)$_2$NMe$_2$]Fe-(η^5-C$_5$H$_5$)}Cl] (**2a**). The other solid, which was obtained after the elution with a CH$_2$Cl$_2$/MeOH mixture (100/1), was characterized by elemental analyses, FAB$^+$ mass spectra, and infrared spectroscopy as well as one- and two-dimensional NMR spectroscopy. All these data were consistent with those expected for [Pd{[(PhC=CPh)$_2$(η^5-C$_5$H$_3$)CH=N(CH$_2$)$_2$NMe$_2$]Fe(η^5-C$_5$H$_5$)][BF$_4$] (**4a**) (Scheme 2), which arises from the bis insertion of PhC≡CPh. The X-ray crystal structure of this complex (vide infra) confirmed these results as well as the arrangement of the phenyl rings depicted in Scheme 2 and the η^3 mode of binding of the butadienyl unit.

Similarly, the treatment of **2b** in acetone with a 50% excess of Tl[BF$_4$] at room temperature (ca. 20 °C), followed by the removal of the TlCl formed and the excess of Tl[BF$_4$], gave (after concentration to dryness) a red-brown residue, hereinafter referred to as **3b**. Further treatment of **3b** with PhC≡CPh (in a alkyne/palladium(II) molar ratio of 2) in refluxing CH$_2$Cl$_2$ for 2 h led, after workup of the column, to unreacted **2b** and an additional orange-red solid which was identified on the basis of elemental analyses, mass spectrometry, and infrared and NMR spectra (see Experimental Section), as well as by X-ray diffraction (vide infra), as [Pd-{[(PhC=CPh)$_2$(η^5-C$_5$H$_3$)CH=N(CH$_2$)$_3$NMe$_2$]Fe(η^5-C$_5$H$_5$)}]-[BF$_4$] (**4b**) (Chart 2).

It should be noted that the yields of **4a** and **4b** were clearly smaller than those reported for [Pd{[(R^{1}C=CR^1)$_2$-(η^5-C$_5$H$_3$)C(R^2)=NR^3]Fe(η^5-C$_5$H$_5$)}Cl] described previously.[12]

When the reactions were performed under identical experimental conditions but using hex-3-yne and **2a** (or **2b**) as starting materials, two palladium(II) compounds were also isolated in each case; one of them was the unreacted cyclopalladated derivative **2a** or **2b**, while the other was identified according to elemental analyses, mass spectra (FAB$^+$), and infrared and NMR spectroscopy as [Pd{[(EtC=CEt)$_2$(η^5-C$_5$H$_3$)CH=N(CH$_2$)$_n$NMe$_2$]-Fe(η^5-C$_5$H$_5$)}][BF$_4$] (n = 2 (**5a**), 3 (**5b**) (Scheme 2 and Chart 2, respectively)), which arise from the bis insertion of the hex-3-yne into the σ[Pd−C(sp^2,ferrocene)] bond. The X-ray crystal structure of **5b** (see below) confirmed the arrangement of the ethyl groups depicted in Chart 2 and a η^3 mode of binding of the butadienyl unit. It should be noted that the yield of **5a** was very low when the refluxing period was equal to 2 h, but it could be improved by using longer reaction periods (6 h). This result suggests that for **2b** the bis insertion of the hex-3-yne requires milder experimental conditions than for **2a**.

Chart 2



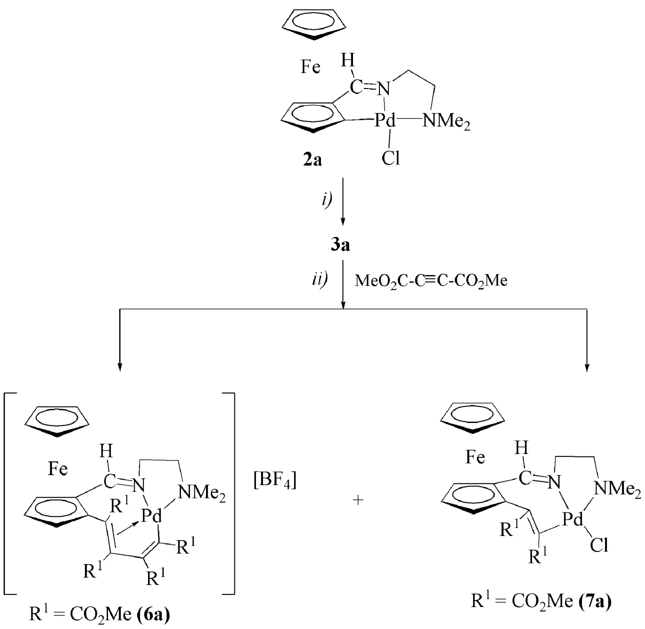
R^1 = Ph (4b) or Et (5b)

In these reactions the amounts of **2a** or **2b** recovered did not vary significantly when (a) longer refluxing periods (up to 10 h) were used or (b) the starting materials **2** were treated with Tl[BF$_4$] in tetrahydrofuran prior to the addition of the alkyne.

More interesting are the results obtained in the reactions of **2a** with MeO$_2$CC≡CCO$_2$Me under identical experimental conditions. In this case the compounds [Pd{[(MeO$_2$CC=CCO$_2$Me)$_2$(η^5-C$_5$H$_3$)CH=N(CH$_2$)$_2$NMe$_2$]-Fe(η^5-C$_5$H$_5$)}][BF$_4$] (**6a**) and [Pd{[(MeO$_2$CC=CCO$_2$Me)-(η^5-C$_5$H$_3$)CH=N(CH$_2$)$_n$NMe$_2$]Fe(η^5-C$_5$H$_5$)}Cl] (**7a**) were obtained exclusively (Scheme 3) and no evidence for the presence of unreacted **2a** was detected by NMR spectroscopy. The deep orange complex **6a** formed by the bis insertion of the alkyne and its cationic array is similar to those of **4a** and **5a**, except for the nature of the substituents R^1 on the η^3-butadienyl fragment, while compound **7a**, which is a bright yellow solid, contains a seven-membered palladacycle formed by the insertion of one molecule of MeO$_2$CC≡CCO$_2$Me.

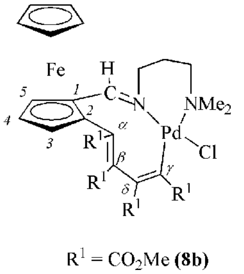
When the reaction was performed under identical experimental conditions, but using **2b** (269 mg) as starting material, three compounds could be isolated, after the workup of the SiO$_2$ column. The first eluted band produced a yellow product whose characterization data agreed with those expected for [Pd{[(MeO$_2$CC=CCO$_2$Me)(η^5-C$_5$H$_3$)CH=N(CH$_2$)$_3$NMe$_2$]Fe(η^5-C$_5$H$_5$)}Cl] (**7b**). A small amount (~15 mg) of another yellow complex (hereinafter referred to as **8b**) was obtained after concentration of the second eluted band, and its elemental analyses, mass spectrometry, and IR and NMR spectra were consistent with those of [Pd{[(MeO$_2$-CC=CCO$_2$Me)$_2$(η^5-C$_5$H$_3$)CH=N(CH$_2$)$_3$NMe$_2$]Fe(η^5-C$_5$H$_5$)}-Cl] (**8b**) (Chart 3), which arises from the bis insertion of the alkyne into the σ[Pd−C(sp^2,ferrocene)] bond. The crystal structure of **8b** (vide infra) reveals an η^1 mode

Scheme 3[a]



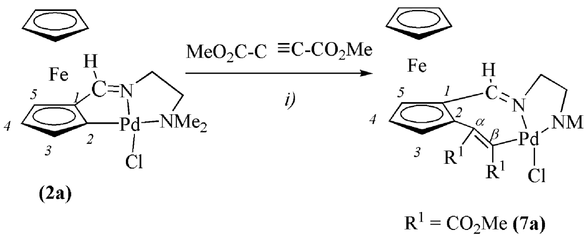
[a] Legend: (i) $Tl[BF_4]$ in acetone; (ii) in a alkyne/Pd molar ratio of 2, in refluxing CH_2Cl_2, followed by SiO_2 column chromatography (see text).

Chart 3



of binding of the inserted butadienyl unit and the cis arrangement of the $-CO_2Me$ substituents in the two $>C=C<$ groups, shown in Chart 3. The third component was obtained after the elution of the column with a $CH_2Cl_2/MeOH$ (100/1.5) mixture. This produced the release of a deep violet band, which led after concentration to dryness to a purple solid. Its infrared spectrum showed the typical bands of the $[BF_4]^-$ anion,[17] and its FAB^+ mass spectrum showed a peak at *m*/*z* 688, which could be ascribed to the "$[Pd\{[(MeO_2CC=CCO_2Me)_2(\eta^5\text{-}C_5H_3)CH=N(CH_2)_3NMe_2]Fe(\eta^5\text{-}C_5H_5)\}]^+$" cation. In addition, its ^1H and $^{13}C\{^1H\}$ NMR spectroscopic data were very similar to those of **6a**, except for the presence of additional multiplets due to the protons of the central methylene unit of the "$=N(CH_2)_3NMe_2$" moiety. On this basis, we tentatively propose for this complex the formula $[Pd\{[(MeO_2CC=CCO_2Me)_2(\eta^5\text{-}C_5H_3)CH=N\text{-}(CH_2)_3NMe_2]Fe(\eta^5\text{-}C_5H_5)\}][BF_4]$ (**6b**). Attempts to characterize **6b** by elemental analyses failed, due to the low stability of this product in the solid state. The purple color of a freshly prepared solid sample of **6b** turned brownish in a few hours, and its solubility in $CHCl_3$ decreased substantially. A similar change of color was observed in $CHCl_3$ solutions, and the ^1H NMR spectrum of **6b** (in $CDCl_3$) changed with time. Initially, the spectrum of a freshly prepared sample showed a singlet at δ 8.52 ppm, but after 2 days of storage at ca. 20 °C, a group of five singlets at δ 8.84, 8.52, 7.96, 7.92, and 7.74 ppm of relative intensities 1/1.8/0.7/1.2/1.7 could be detected. For longer periods (10 days) the intensity of the signal at δ 7.74 ppm increased while that due to the imine proton of **6b** (at δ 8.52 ppm) vanished, as did the other resonances of **6b**. In addition, a considerable widening of the remaining signals was also observed. These findings suggested that a chemical change involving the decomposition of **6b** was occurring. This type of behavior was not observed for **6a**, in which the chelate is a five-membered ring, thus indicating that the incorporation of an additional $-CH_2-$ fragment in the backbone reduces the stability of the compounds $[Pd\{[(MeO_2CC=CCO_2Me)_2(\eta^5\text{-}C_5H_3)CH=N(CH_2)_nNMe_2]Fe(\eta^5\text{-}C_5H_5)\}][BF_4]$ (n = 2, 3).

Scheme 4[a]



[a] Legend: (*i*) equimolar amount of the alkyne, in refluxing CH_2Cl_2 (21 h) followed by SiO_2 column chromatography.

On the other hand, it is interesting to point out that in the reactions of **2** with $MeO_2CC{\equiv}CCO_2Me$ no evidence for the presence of the starting cyclopalladated complex was detected by NMR spectroscopy. This finding is in sharp contrast with that obtained when the reactions were carried out using diphenylacetylene or hex-3-yne and may be ascribed to the greater reactivity of $MeO_2CC{\equiv}CCO_2Me$ when compared with that of $EtC{\equiv}CEt$ or $PhC{\equiv}CPh$.[18]

Compounds **7** could be isolated in a higher yield when the corresponding complex (**2a** or **2b**) was treated with an equimolar amount of $MeO_2CC{\equiv}CCO_2Me$ in refluxing CH_2Cl_2 and subsequently purified by SiO_2 column chromatography (Scheme 4). It is worth remarking that complex **7b** could be isolated after 6 h of reflux, but for **7a**, the NMR spectrum of the crude product obtained after this refluxing period indicated the presence of the starting material **2a** and **7a** in the molar ratio **2a**/**7a** = 6. However, an increase of the refluxing period (up to 21 h) produced a decrease of the relative proportion **2a**/**7a**. These results suggest that **2a** is less reactive than **2b** versus the alkyne $MeO_2CC{\equiv}CCO_2Me$.

However, when the reaction was performed using **2b** and $MeO_2CC{\equiv}CCO_2Me$ (in a 1/2 molar ratio), compound **7b** was isolated and the formation of traces of the bis insertion derivative **8b** was also detected by NMR spectroscopy. In contrast with these results, when the reaction was carried out using **2a** as reagent and longer reaction periods (up to 4 days), the presence of

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[17] Nakamoto, K. *IR and Raman Spectra of Inorganic and Coordination Compounds*, 5th ed.; Wiley: New York, 1997.

[18] (a) *Houben-Weyl: Methoden der Organische Chemie: Alkine, Di und Polyne, Kumulene*; Müller, E., Jäger, V., Murray, M., Niedballa, V., Eds.; Georg Thieme Verlag: Stuttgart, Germany, 1977; Vol. 5/2a, p 33. (b) *Comprehensive Organic Chemistry: The Synthesis and Reactions of Organic Compounds*, Barton, D., Ollis, W. D., Eds.; Pergamon: Exeter, U.K., 1979; Vol. 1, p 193.

$[Pd\{[(MeO_2CC{=}CCO_2Me)_2(\eta^5\text{-}C_5H_3)CH{=}N(CH_2)_2NMe_2]\text{-}Fe(\eta^5\text{-}C_5H_5)\}Cl]$ (**8a**) was not detected.

In the view of these findings and in order to elucidate if compound **7b** could be an intermediate species in the formation of **8b**, we also studied the reaction between equimolar amounts of **7b** and $MeO_2CC{\equiv}CCO_2Me$ in refluxing CH_2Cl_2 under different refluxing periods (up to 3 days). However, no evidence for the presence of **8b** in the reaction mixture was detected by NMR spectroscopy. These findings indicate that the insertion of an additional molecule of $MeO_2CC{\equiv}CCO_2Me$ into the σ-(Pd−C) bond of **7b** is unlikely to occur under these experimental conditions, thus suggesting that complex **8b** may be generated through a different pathway.

Characterization. All the compounds presented in this work have been characterized by elemental analyses (except complex **6b**, which exhibits low stability in the solid state), FAB$^+$ mass spectrometry, and infrared and one- and two-dimensional NMR spectroscopy, and compounds **4a**,**b**, **5b**, and **8b** have also been characterized by X-ray diffraction.

In all cases the elemental analyses agreed with the proposed formulas (see the Experimental Section). The infrared spectra of all the compounds showed a sharp and intense band in the range 1500−1650 cm^{-1}, which is ascribed to the stretching of the $>C{=}N$ group.[19] This band appears at higher energies than for the five-membered cyclopalladated complexes **2**.[13,14] For the ionic derivatives, **4a**,**b**−**6a**,**b** the typical bands of the $[BF_4]^-$ anion[17] were also observed in the infrared spectra.

Proton and carbon-13 NMR spectroscopic data for all the compounds is presented in the Experimental Section, and in all cases the assignment of the signals has been carried out with the aid of two-dimensional heteronuclear $\{^1H-^{13}C\}$ experiments (HSQC and HMBC). ^1H NMR spectra of all the compounds showed a group of four signals of relative intensities 1/1/1/5 in the range 3.5−5.2 ppm, which is the typical pattern of 1,2-disubstituted ferrocenes.[20] The resonance of the imine proton appeared as a singlet in the low-field region of the spectra, and signals due to the protons of the two (in **7**) or four (in **4a**,**b; 6a**,**b**, and **8b**) R^1 groups of the inserted fragment were identified in the spectra. However, the high-field regions of the ^1H NMR spectra of $[Pd\{[(EtC{=}CEt)_2(\eta^5\text{-}C_5H_3)CH{=}N(CH_2)_nNMe_2]Fe(\eta^5\text{-}C_5H_5)\}][BF_4]$ (n = 2 (**5a**), 3 (**5b**)) were complex. In these cases, the signals due to the protons of the $-CH_2-$ moieties of the "$=N(CH_2)_nNMe_2$" fragment overlapped with those of the methylenic protons of the ethyl groups belonging to the η^3-butadienyl fragments, and the assignment of these signals could only be achieved with the aid of the two-dimensional $\{^1H-^{13}C\}$ NMR experiments.

$^{13}C\{^1H\}$ NMR spectra of all the compounds were also recorded (see the Experimental Section). The resonance of the imine carbon appeared in the range 160−170 ppm and was easily identified with the aid of two-dimensional HSQC experiments, and in most of the cases the signals due to the quaternary carbons of the inserted fragment were also observed in the range 90−150 ppm as low intense signals.

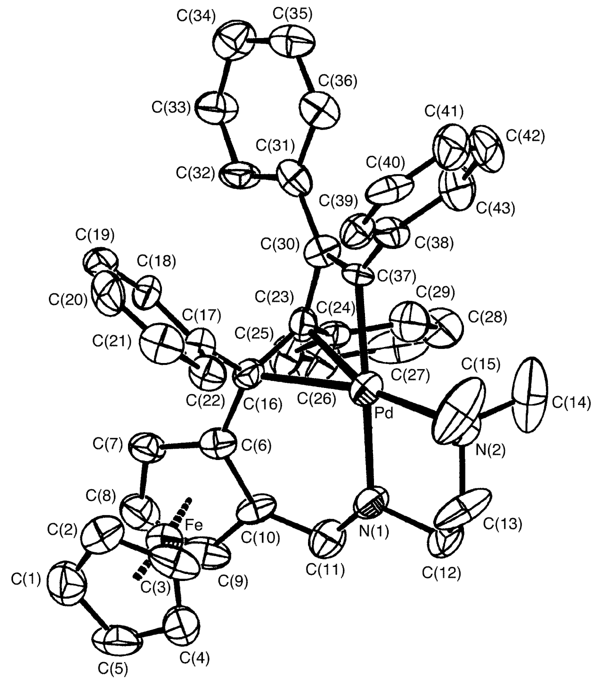

Figure 1. ORTEP diagram of the cationic array of $[Pd\{[(PhC{=}CPh)_2(\eta^5\text{-}C_5H_3)CH{=}N(CH_2)_2NMe_2]Fe(\eta^5\text{-}C_5H_5)]\text{-}[BF_4]\cdot CH_2Cl_2$ (**4a**) together with the numbering scheme. Hydrogen atoms have been omitted for clarity.

The resonances due to the carbon-13 nuclei of the −Et or −OMe groups of the R^1 substituents (in compounds **5a**,**b**−**7a**,**b** and **8**) were easily identified in the high-field region of the spectra and provided additional evidence of the incorporation of one (in **7a**,**b**) or two (in **5a**,**b**, **6a**,**b**, and **8b**) molecules of the alkyne into the σ-[Pd−C(sp^2,ferrocene)] bond. The positions of the signals were in good agreement with the results reported for related palladacycles arising from mono or bis insertion of the alkynes under study into the σ[Pd−C(sp^2, ferrocene)] (of **1**) or the σ[Pd−C(sp^2,aryl)] bond having a similar arrangement of the R^1 groups.[8,12]

Description of the Crystal Structures of $[Pd\{[(PhC{=}CPh)_2(\eta^5\text{-}C_5H_3)CH{=}N(CH_2)_nNMe_2]Fe(\eta^5\text{-}C_5H_5)\}][BF_4]\cdot CH_2Cl_2$ (n = 2 (4a), 3 (4b)). The X-ray crystal structures of these compounds consist of equimolar amounts of the heterobimetallic cations $[Pd\{[(PhC{=}CPh)_2(\eta^5\text{-}C_5H_3)CH{=}N(CH_2)_nNMe_2]Fe(\eta^5\text{-}C_5H_5)\}]^+$ (n = 2 (**4a**), 3 (**4b**)), the $[BF_4]^-$ anion, and CH_2Cl_2.

Perspective drawings of the cationic arrays of **4a**,**b** are depicted in Figures 1 and 2, respectively, and a summary of the most relevant bond lengths and angles is presented in Tables 2 and 3.

In the two cases, the palladium is four-coordinate, since it is bound to the two nitrogen atoms of the ferrocenylaldimine (N(1) and N(2)), to the terminal carbon of the η^3-butadienyl unit (C(37) in **4a** and C(20) in **4b**), and to the middle point of the segment defined by the atoms C(16) and C(23) in **4a** or C(17)−C(18) in **4b** (hereinafter referred to as χ and χ') in a slightly

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[19] (a) Onue, H.; Moritani, I. *J. Organomet. Chem.* **1972**, *43*, 431. (b) Onue, H.; Nakagawa, K. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 3480. (c) Albert, J.; Granell, J.; Sales, J.; Solans, X.; Font-Bardía, M. *Organometallics* **1986**, *5*, 2567. (d) Crespo, M.; Solans, X.; Font-Bardía, M. *Organometallics* **1995**, *14*, 355. (e) Wu, Y. L.; Ding, L.; Wang, H. Y.; Liu, Y. H.; Yuan, H. Z.; Mao, X. A. *J. Organomet. Chem.* **1997**, *535*, 49.

[20] *Gmelin Handuch der Anorganische Chemie. Eisen Organische-Verbindunge. Ferrocen;* Springer-Verlag: Heidelberg, Germany, 1977-1986; Part A1-A8.

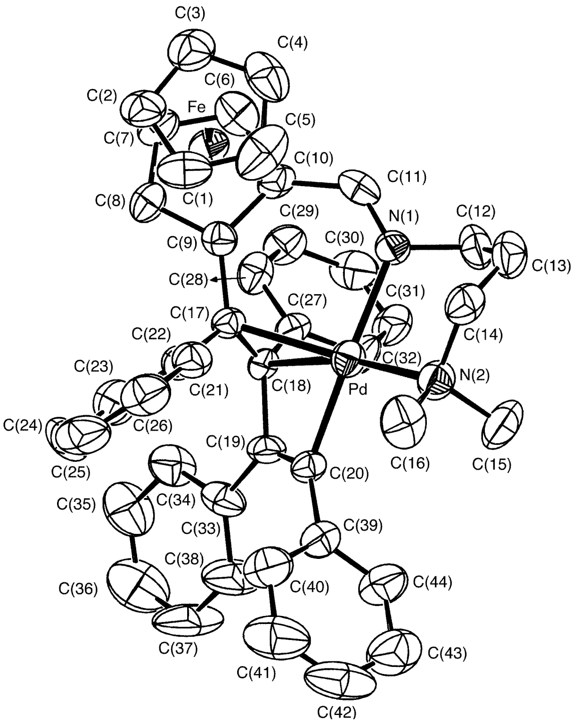

Figure 2. Molecular structure of the cationic array of [Pd{[(PhC=CPh)$_2$(η^5-C$_5$H$_3$)CH=N(CH$_2$)$_3$NMe$_2$]Fe(η^5-C$_5$H$_5$)]-[BF$_4$]·CH$_2$Cl$_2$ (**4b**) together with the numbering scheme. Hydrogen atoms have been omitted for clarity.

Table 2. Selected Bond Lengths (in Å) and Bond Angles (in deg) for [Pd{[(PhC=CPh)$_2$(η^5-C$_5$H$_3$)-CH=N(CH$_2$)$_2$NMe$_2$]Fe(η^5-C$_5$H$_5$)}][BF$_4$]·CH$_2$Cl$_2$ (4a)[a]

Selected Bond Lengths			
Pd−N(1)	2.144(7)	Pd−N(2)	2.103(7)
Pd−C(37)	2.040(7)	Pd−C(23)	2.116(7)
Pd−C(16)	2.239(7)	Pd−χ^b	2.066(7)
Pd−C(30)	2.614(7)	N(1)−C(11)	1.283(10)
C(6)−C(16)	1.513(11)	C(16)−C(23)	1.417(9)
C(23)−C(30)	1.501(10)	C(30)−C(37)	1.343(9)
C(17)−C(16)	1.518(10)	C(24)−C(23)	1.481(10)
C(31)−C(30)	1.454(10)	C(38)−C(37)	1.428(10)
N(1)−C(12)	1.518(10)	N(2)−C(15)	1.442(11)
N(2)−C(14)	1.449(12)	N(2)−C(13)	1.474(13)
Fe−C^b	2.027(32)	C−C^c	1.374(34)
Selected Bond Angles			
C(37)−Pd−N(2)	104.0(3)	N(2)−Pd−N(1)	81.8(3)
N(1)−Pd−χ^b	119.6(3)	C(37)−Pd−χ^b	74.2(3)
N(1)−Pd−C(16)	91.4(3)	C(37)−Pd-C(23)	65.3(3)
C(37)−Pd−C(16)	84.1(3)	Pd−N(1)−C(11)	130.9(6)
N(1)−C(11)−C(10)	122.4(9)	C(11)−C(10)−C(6)	129.6(8)
C(10)−C(6)−C(16)	129.2(7)	C(6)−C(16)−C(23)	121.7(7)
C(16)−C(23)−C(30)	118.1(7)	C(23)−C(30)−C(37)	104.0(6)
C(30)−C(37)−Pd	99.1(5)	Pd−N(1)−C(12)	108.7(5)
C(12)−C(13)−N(2)	114.0(10)	C(13)−N(2)−Pd	106.5(6)
C(11)−C(10)−C(9)	121.5(8)	C(7)−C(6)−C(16)	124.4(8)
C(6)−C(16)−C(17)	115.4(5)	C(17)−C(16)−C(23)	119.8(7)
C(16)−C(23)−C(24)	122.9(7)	C(30)−C(23)−C(24)	118.3(5)
C(23)−C(30)−C(31)	120.7(6)	C(31)−C(30)−C(37)	134.7(7)
C(30)−C(37)−C(38)	131.2(7)	C(38)−C(37)−Pd	129.2(5)

[a] Standard deviation parameters are given in parentheses. [b] χ represents the middle point of the segment defined by the atoms C(16) and C(23). [c] Average value for the ferrocenyl moiety.

Table 3. Selected Bond Lengths (in Å) and Bond Angles (in deg) for [Pd{[(PhC=CPh)$_2$(η^5-C$_5$H$_3$)-CH=N(CH$_2$)$_3$NMe$_2$]Fe(η^5-C$_5$H$_5$)}][BF$_4$]·CH$_2$Cl$_2$ (4b)[a]

Selected Bond Lengths			
Pd−N(1)	2.113(3)	Pd−N(2)	2.141(3)
Pd−C(20)	2.030(4)	Pd−C(18)	2.166(3)
Pd−C(17)	2.250(3)	Pd−χ^b	2.090(3)
Pd−C(19)	2.552(4)	N(1)−C(11)	1.261(5)
C(9)−C(17)	1.478(5)	C(17)−C(18)	1.422(4)
C(18)−C(19)	1.491(5)	C(19)−C(20)	1.331(5)
C(17)−C(21)	1.495(4)	C(18)−C(27)	1.487(5)
C(19)−C(33)	1.518(6)	C(20)−C(39)	1.438(6)
N(1)−C(12)	1.459(4)	C(12)−C(13)	1.526(6)
C(13)−C(14)	1.498(6)	C(14)−N(2)	1.514(6)
N(2)−C(15)	1.486(4)	N(2)−C(16)	1.464(5)
Fe−C^c	2.041(21)	C−C^c	1.405(22)
Selected Bond Angles			
C(20)−Pd−N(2)	101.6(2)	N(2)−Pd−N(1)	89.9(1)
N(1)−Pd−χ^b	96.9(2)	C(20)−Pd−χ^b	75.0(2)
N(1)−Pd−C(17)	93.0(1)	C(20)−Pd−C(18)	66.6(2)
Pd−N(2)−C(14)	109.0(3)	N(2)−C(14)−C(13)	116.7(4)
C(14)−C(13)−C(12)	115.4(4)	C(13)−C(12)−N(1)	111.0(3)
C(12)−N(1)−C(11)	116.8(4)	N(1)−C(11)−C(10)	123.4(4)
C(11)−C(10)−C(9)	128.9(4)	C(10)−C(9)−C(17)	128.5(3)
C(9)−C(17)−C(18)	120.5(3)	C(17)−C(18)−C(19)	116.1(3)
C(18)−C(19)−C(20)	109.4(4)	C(19)−C(20)−Pd	96.6(3)
C(16)−N(2)−Pd	108.6(2)	C(15)−N(2)−Pd	114.9(3)

[a] Standard deviation parameters are given in parentheses. [b] χ' represents the middle point of the segment defined by the atoms C(17) and C(18). [c] Average value for the ferrocenyl moiety.

distorted square-planar environment.[21] In both cases the Pd−N and the Pd−C bond lengths are similar to those found in five-membered cyclopalladated complexes.[22]

The double bond of the η^3-butadienyl unit fragment closest to the ferrocenyl unit is bound unsymmetrically to the palladium(II), as reflected in the two Pd−C bond lengths (2.116(7) and 2.239(7) Å, respectively (in **4a**), or 2.166(3) and 2.250(4) Å (in **4b**)). This arrangement, also detected in [Pd{[(PhC=CPh)$_2$(η^5-C$_5$H$_3$)CH=NCH$_2$-Ph]Fe(η^5-C$_5$H$_5$)}Cl],[12a] is different from those reported for most nine-membered metallacycles arising from the bis insertion of alkynes.[11,12,23]

In **4a** the C(30)−C(37) bond distance is clearly shorter (1.343(9) Å) than that of the C(16)−C(23) double bond (1.417(9) Å), and a similar trend is also found between the C(19)−C(20) and C(17)−C(18) bond distances in **4b**. These differences can be attributed to the different type of coordinations of the two >C=C< double bonds to the palladium(II) atom (η^1 and η^2), respectively.

The cationic arrays of these compounds contain a [5,9,5] (in **4a**) or a [5,9,6] (in **4b**) tricyclic system formed by the fusion of the substituted pentagonal ring of the ferrocenyl moiety, a nine-membered metallacycle, and a five- (in **4a**) or six-membered chelate ring (in **4b**).

In the two compounds, the >C=N− functional group is contained in the nine-membered metallacycles (endocyclic), and the >C=N− bond lengths (1.283(10) Å in **4a** and 1.261(5) Å in **4b**) do not differ significantly from the values reported for *cis*-[M{[(η^5-C$_5$H$_4$)CH=N(CH$_2$)$_n$-

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(21) (a) For **4a**, the least-squares equation of the plane defined by the atoms N(1), N(2), C(37), and χ is (0.1841)XO + (0.8246)YO + (0.5350)ZO = 7.6792. Deviations from the plane (Å): N(1), −0.023; N(2), 0.022; C(37), −0.025; χ, 0.025. (b) In **4b** the least-squares equation of the plane defined by the atoms N(1), N(2), C(20), and χ' is (−0.1459) XO + (0.9747)YO + (0.1693)ZO = 1.2626. Deviations from the main plane (Å): N(1), 0.229; N(2), −0.223; C(20), 0.273; χ', −0.280.

(22) (a) López, C.; Sales, J.; Solans, X.; Zquiak, R. *J. Chem. Soc., Dalton Trans.* **1992**, 2321. (b) Bosque, R.; López, C.; Sales, J.; Solans, X. Font-Bardía, M. *J. Chem. Soc., Dalton Trans.* **1994**, 735. (c) Bosque, R.; Font-Bardía, M.; López, C.; Silver, J.; Solans, X. *J. Chem. Soc., Dalton Trans.* **1994**, 747. (d) Bosque, R.; López, C.; Sales, J.; Solans, X. *J. Organomet. Chem.* **1994**, *483*, 61. (e) López, C.; Bosque, R.; Solans, X.; Font-Bardía, M. *New J. Chem.* **1998**, *22*, 977.

(23) (a) Albinati, A.; Pregosin, P. S.; Rüedi, R. *Helv. Chim. Acta*, **1985**, *68*, 2064. (b) Maassarani, F.; Pfeffer, M.; Le Borgne, G. *Organometallics* **1987**, *6*, 2029. (c) Maassarani, F.; Pfeffer, M.; van Koten, G. *Organometallics* **1989**, *8*, 871. (d) Albert, J.; Granell, J.; Sales, J.; Solans, X. *J. Organomet. Chem.* **1989**, *379*, 177.

$NMe_2]Fe(\eta^5\text{-}C_5H_5)\}Cl_2]$, ($n$ = 2, 3 and M = Pd, Zn)[14,24] or the cyclopalladated complexes $[Pd\{[(\eta^5\text{-}C_5H_3)CH{=}N(CH_2)_nNMe_2]Fe(\eta^5\text{-}C_5H_5)\}Cl]$ (1.260(11) Å for n = 2 (**2a**) and 1.268(8) Å for n = 3 (**2b**)).[14,25]

In **4a** the phenyl substituents on the double bond C(16)−C(23) are trans to each other and those on the C(30)−C(37) are cis and a similar arrangement of the phenyl rings is found for **4b**. This is the most common distribution of substituents found in related palladacycles.[11,12,23]

The C(16)−C(23) bond (in **4a**) or the C(17)−C(18) bond (in **4b**) of the butadienyl unit is located above the plane defined by the atoms (C(6)−C(10)) opposite to the "$Fe(\eta^5\text{-}C_5H_5)$" unit, and the phenyl bound to the C(16) atom in **4a** or to the C(17) atom in **4b** is oriented toward the iron(II). This type of arrangement is similar to those found in $[Pd\{[(PhC{=}CPh)_2(\eta^3\text{-}C_5H_3)C(R^2){=}NR^3]Fe(\eta^5\text{-}C_5H_5)\}Cl]$ (R^2 = H, Me, Ph and R^3 = Ph, CH_2Ph).[2c,12a]

In **4a**, the five-membered chelate ring, formed by the atoms Pd, N(1), N(2), C(12), and C(13), has an envelope-like conformation,[26] while the six-membered ring in **4b** exhibits a twist-boat conformation.[27]

In complex **4a** the $[BF_4]^-$ anion was found in disordered positions, and in complex **4b** the analysis of the X-ray data suggests weak C−H···F interactions[28] involving the sets of atoms C(4)−H(4)···F(23), C(11)−H(11)···F(24), and C(15)−H(15A)···F(22). In addition to this finding, the separation between the centroid of the C_5H_5 and the C(13)−H(13) bond (2.784 Å) of a neighboring cation indicate, according to the literature,[29] the existence of two weak C−H···π(ring) interactions. A similar feature is found between the phenyl ring, formed by the atoms C(33)−C(38), and the C(41)−H(41) bond (3.095 Å) of a close cation.

Description of the Crystal Structure of $[Pd\{[(EtC{=}CEt)_2(\eta^5\text{-}C_5H_3)CH{=}N(CH_2)_3NMe_2]Fe(\eta^5\text{-}C_5H_5)\}][BF_4]\cdot CH_2Cl_2$ (5b). The X-ray crystal structure consists of equimolar amounts of the cation $[Pd\{[(EtC{=}CEt)_2(\eta^5\text{-}C_5H_3)CH{=}N(CH_2)_3NMe_2]Fe(\eta^5\text{-}C_5H_5)\}]^+$ and the $[BF_4]^-$ anion. A perspective drawing of the cationic array is depicted in Figure 3, and a summary of the most relevant bond lengths and angles is presented in Table 4.

In the cation the palladium is bound to the two nitrogen atoms (N(1) and N(2)), to the terminal carbon of the η^3-butadienyl unit (C(26)), and to the middle point of the segment defined by the atoms C(17) and C(20) (hereinafter referred to as χ''). A slightly distorted square planar environment is the result.[30] The cation contains a [5,9,6] tricyclic system formed by the fusion of the substituted pentagonal ring of the ferrocenyl moiety, a nine-membered metallacycle, and a six-membered chelate ring. The nine-membered metallacycle contains the imine group (endocyclic).

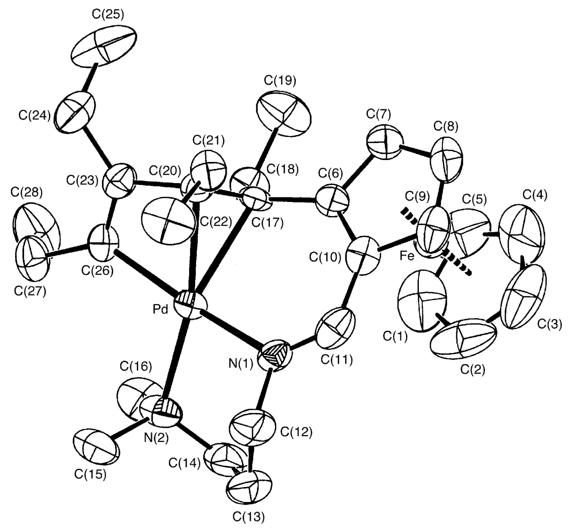

Figure 3. Molecular structure of the cationic array of $[Pd\{[(EtC{=}CEt)_2(\eta^5\text{-}C_5H_3)CH{=}N(CH_2)_3NMe_2]Fe(\eta^5\text{-}C_5H_5)]\text{-}[BF_4]\cdot CH_2Cl_2$ (**5b**) together with the atom-labeling scheme. Hydrogen atoms have been omitted for clarity.

Table 4. Selected Bond Lengths (in Å) and Bond Angles (in deg) for $[Pd\{[(EtC{=}CEt)_2\text{-}(\eta^5\text{-}C_5H_3)CH{=}N(CH_2)_3NMe_2]Fe(\eta^5\text{-}C_5H_5)\}][BF_4]$ (5b)[a]

Selected Bond Lengths			
Pd−N(1)	2.118(3)	Pd−N(2)	2.150(5)
Pd−C(26)	2.012(4)	Pd−C(20)	2.214(5)
Pd−C(17)	2.255(5)	Pd−χ^b	1.980(5)
Pd−C(23)	2.579(5)	N(1)−C(11)	1.269(11)
C(6)−C(17)	1.499(7)	C(17)−C(18)	1.525(7)
C(17)−C(20)	1.401(7)	C(20)−C(21)	1.516(7)
C(20)−C(23)	1.503(7)	C(23)−C(24)	1.503(8)
C(23)−C(26)	1.320(8)	C(26)−C(27)	1.511(7)
N(1)−C(12)	1.472(11)	C(12)−C(13)	1.518(12)
C(13)−C(14)	1.520(11)	N(2)−C(15)	1.488(9)
N(2)−C(14)	1.479(8)	N(2)−C(16)	1.482(8)
Fe−C^c	2.033(13)	C−C^c	1.401(34)

Selected Bond Angles			
C(26)−Pd−N(2)	101.7(2)	N(2)−Pd−N(1)	89.4(3)
N(1)−Pd−χ^b	98.6(2)	C(26)−Pd−χ^b	74.7(2)
Pd−N(1)−C(11)	128.7(6)	N(1)−C(11)−C(10)	125.2(6)
C(11)−C(10)−C(6)	129.5(5)	C(10)−C(6)−C(17)	127.4(5)
C(6)−C(17)−C(20)	117.6(4)	C(17)−C(20)−C(23)	119.9(4)
C(20)−C(23)−C(26)	108.4(4)	Pd−N(2)−C(14)	108.3(4)
N(2)−C(14)−C(13)	116.9(6)	C(14)−C(13)−C(12)	114.5(6)
C(13)−C(12)−N(1)	111.4(6)	C(12)−N(1)−C(11)	117.0(5)
C(15)−N(2)−Pd	114.4(4)	C(16)−N(2)−C(14)	107.2(4)

[a] Standard deviation parameters are given in parentheses. [b] χ'' represents the middle point of the segment defined by the atoms C(17) and C(20). [c] Average value for the ferrocenyl moiety.

As described for **4b**, also in this case the double bond of the η^3-butadienyl unit fragment closest to the ferrocenyl unit (C(17)−C(20)) is bound unsymmetrically to the palladium(II), as reflected in the two Pd−C bond lengths (2.214(5) and 2.255(5) Å, respectively), and the Pd−C(26) bond length (2.012(4) Å) is shorter, if significant, than the Pd−C(20) bond distance (2.030(4) Å) of **4b**. The arrangement of the ethyl groups on the η^3-butadienyl fragment is similar to that found for **4b** as well as in $[Pd\{[(EtC{=}CEt)_2(\eta^5\text{-}C_5H_3)C(R^2){=}NR^3]Fe(\eta^5\text{-}C_5H_5)\}Cl]$.[12a,e]

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(24) (a) Bosque, R.; Caubet, A.; López, C.; Espinosa, E.; Molins, E. *J. Organomet. Chem.* **1997**, *544*, 233. (b) López, C.; Caubet, A.; Pérez, S.; Bosque, R.; Solans, X.; Font-Bardía, M. *Polyhedron* **2002**, *21*, 2361.

(25) (a) López, C.; Pawełczyk, A.; Solans, X.; Font-Bardía, M. *Inorg. Chem. Commun.* **2003**, *6*, 451.

(26) The least-squares equation of the plane defined by the atoms Pd, N(1), N(2), and C(12) in **4a** is (0.0626)XO + (0.8145)YO + (0.5768) YO = 6.7269. Deviations from the main plane (Å): Pd, −0.065; N(1), 0.090; N(2), 0.054; C(12), −0.078.

(27) (a) Cremer, D.; Pople, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 1354. (b) Boeyens, J. C. A. *J. Cryst. Mol. Struct.* **1978**, *8*, 317.

(28) Le, H.; Knobler, C. B.; Hawthorne, M. F. *Chem. Commun.* **2000**, 2485.

(29) Nishio, N.; Hirota, M.; Umezakwo, Y. *The C−H·····π Interaction*; Wiley-VCH: New York, 1988.

(30) The least-squares equation of the plane defined by the atoms Pd, N(1), N(2), C(26), and the middle point of the segment C(17)−C(20) (χ'') in **5b** is (0.9152)XO + (−0.3931)YO + (−0.0893)ZO = 3.5800. Deviations from the plane (Å): N(1), 0.390; N(2), −0.372; C(26), 0.456; χ'', −0.483.

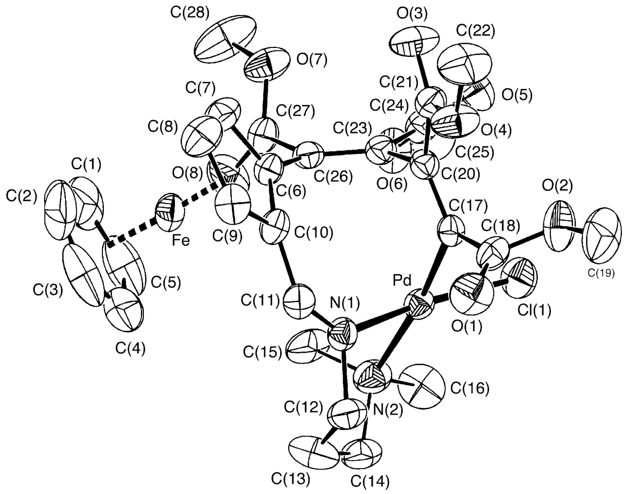

Figure 4. Molecular structure and atom-numbering scheme for [Pd{[(MeO$_2$CC═CCO$_2$Me)$_2$(η^5-C$_5$H$_3$)CH═N(CH$_2$)$_3$NMe$_2$]-Fe(η^5-C$_5$H$_5$)}Cl] (**8b**). Hydrogen atoms have been omitted for clarity.

The six-membered chelate ring, formed by the atoms Pd, N(1), N(2), C(12), C(13), and C(14), has a boat conformation.[31] The differences observed in the bond lengths of the two >C═C< bonds of the butadienyl unit (C(17)−C(20) and C(23)−C(26)) can be ascribed to the different modes of binding of these moieties (η^2 and η^1, respectively).

Bond lengths and angles of the [BF$_4$]$^-$ anion in **5b** agree with the values reported for other compounds containing this ion,[32] and the F(4)···H(24) bond lengths (2.4822 Å) suggests a weak C(24)−H(24)···F(4) interaction.[28]

Description of the Crystal Structure of [Pd{[(MeO$_2$CC═CCO$_2$Me)$_2$(η^5-C$_5$H$_3$)CH═N(CH$_2$)$_2$NMe$_2$]-Fe(η^5-C$_5$H$_5$)}Cl] (8b). The crystal structure of **8b** together with the atom-numbering scheme is depicted in Figure 4, and a selection of bond lengths and angles is presented in Table 5.

The structure consists of [Pd{[(MeO$_2$CC═CCO$_2$Me)$_2$-(η^5-C$_5$H$_3$)CH═N(CH$_2$)$_3$NMe$_2$]Fe(η^5-C$_5$H$_5$)}Cl] separated by van der Waals contacts. In each molecule the palladium atom is four-coordinated, since it is bound to a chlorine, the two nitrogen atoms of the ligand (N(1) and N(2)), and the terminal carbon atom of the η^1-butadienyl unit (C(17)). A distorted-square-planar environment is the result.[33] The Pd−Cl bond length (2.3025(6) Å) is shorter than that found for **2a** (2.328(3) Å)[25] or **2b** (2.3143(9) Å).[14]

This complex contains a [5,9,6] tricyclic system which is formed by fusion of the C$_5$H$_3$ ring, a nine-membered palladacycle, and a six-membered chelate ring formed by the coordination of the two nitrogen atoms of the ligand (N(1) and N(2)) to the palladium(II).

The iminic group is contained in the metallacycle (endocyclic), and the >C═N− bond length (1.281(3) Å) is similar to that found for **2** (1.260(11) Å in **2a** and 1.287(5) Å in **2b**)[14,25] and those of related ferrocenylimines which fall in the range 1.25−1.31 Å.[34]

Table 5. Selected Bond Lengths (in Å) and Bond Angles (in deg) for [Pd{[(MeO$_2$CC═CCO$_2$Me)$_2$-(η^5-C$_5$H$_3$)CH═N(CH$_2$)$_3$NMe$_2$]Fe(η^5-C$_5$H$_5$)}Cl] (8b)[a]

	Selected Bond Lengths		
Pd−C(17)	1.982(2)	Pd−N(1)	2.027(2)
Pd−N(2)	2.177(2)	Pd−Cl(1)	2.3025(6)
N(1)−C(11)	1.281(3)	N(1)−C(12)	1.486(3)
C(10)−C(11)	1.451(3)	C(12)−C(13)	1.513(4)
C(6)−C(10)	1.453(3)	C(10)−C(9)	1.442(3)
C(6)−C(26)	1.468(3)	C(26)−C(23)	1.346(3)
C(23)−C(20)	1.497(3)	C(20)−C(17)	1.327(3)
C(26)−C(27)	1.510(3)	C(23)−C(24)	1.498(3)
C(20)−C(21)	1.482(3)	C(17)−C(18)	1.474(3)
Fe−C[b]	2.037(11)	C−C[b]	1.405(30)
	Selected Bond Angles		
C(17)−Pd−N(1)	87.47(8)	N(1)−Pd−N(2)	89.89(8)
C(17)−Pd−Cl(1)	89.54(6)	N(2)−Pd−Cl(1)	94.01(6)
N(1)−C(11)−C(10)	132.0(2)	C(11)−C(10)−C(6)	133.5(2)
C(10)−C(6)−C(26)	123.3(2)	C(6)−C(26)−C(23)	122.0(2)
C(26)−C(23)−C(20)	120.7(2)	C(23)−C(20)−C(17)	118.3(2)
C(20)−C(17)−Pd	115.27(17)	C(18)−C(17)−Pd	119.7(2)

[a] Standard deviation parameters are given in parentheses. [b] Average value for the ferrocenyl moiety.

The most interesting feature of the crystal structure of **8b** is the relative arrangement of the four −CO$_2$Me groups; in this case the two pairs of −CO$_2$Me groups on the >C═C< bonds of the butadienyl fragment are in a cis,cis arrangement, in contrast with the results obtained for most of the palladacycles arising from the bis insertion of the alkynes R^{1}C≡CR^1, in which the four R^1 substituents have a trans,cis orientation.[12] In good agreement with the conclusions reached from the mechanistic studies of the bis insertion of alkynes into the σ-[Pd−C(sp^2,aryl)] bond,[16] which suggested that although in the monoinsertion product the two R^1 groups are in a cis arrangement, the cis → trans isomerization occurs prior to the insertion of the second molecule of the alkyne to produce the bis insertion complex.

For this crystal structure partial disorder affecting the carbon atoms bound to the amine nitrogen was also observed.[35] The separation between the Cl and H(15A) atom of a neighboring molecule (2.715 Å) is shorter than the sum of the van der Waals radii of these atoms (Cl, 1.75 Å; H, 1.20 Å),[36] suggesting a weak C(15)−H(15A)···Cl interaction. [37]

For the four structures described above, bond lengths and angles of the "(η^5-C$_5$H$_5$)Fe(η^5-C$_5$H$_3$)" fragment are consistent with those found for most of the ferrocene derivatives.[32] The two pentagonal rings are planar and nearly parallel (tilt angles 3.06, 7.95, 5.56, and 3.51°

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[31] The least-squares equation of the plane defined by the atoms Pd, N(2), C(12), and C(14) in **5b** is (0.6824)XO + (−0.6786)YO + (0.2715)ZO = 3.0490. Deviations from this plane (Å): Pd, −0.124; N(2), 0.146; C(12), 0.179; C(14), −0.201; N(1), −0.646; C(13), −0.646.

[32] Allen, T. H.; Kennard, O. *Chem. Des. Automat. News* **1993**, *8*, 146.

[33] The least-squares equation of the plane defined by the atoms N(1), N(2), Cl, and C(17) in **8b** is (−0.5653)XO + (0.8243)YO + (0.0278)-ZO = 0.4539. Deviations from the plane (Å): N(1), −0.145; N(2), +0.123; Cl, −0.121; C(17), 0.144 Å.

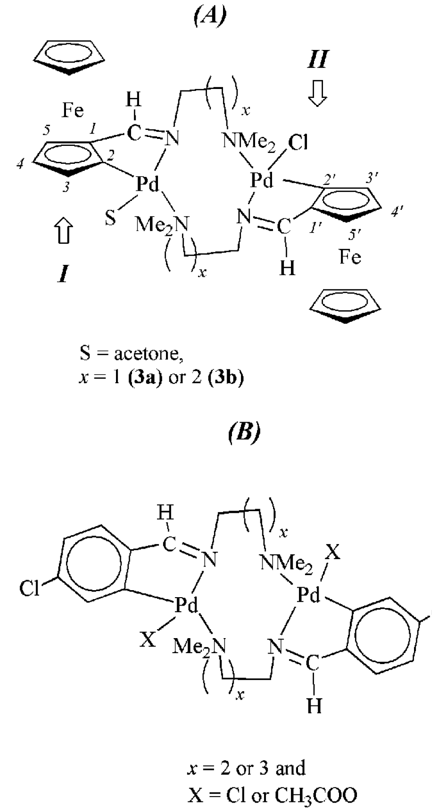
[34] López, C.; Bosque, R.; Solans, X.; Font-Bardía, M. *New J. Chem.* **1996**, *20*, 1285.

[35] The three carbon atoms bound to the amine nitrogen, N(2), showed a slight disorder, and two positions were identified for each of these carbon atoms, which were identified as C(14) and C(14′), C(15) and C(15′), and C(16) and C(16′).

[36] (a) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441. (b) Kitaigorodskii, A. I. *Molecular Crystals and Molecules*; Academic Press: London, 1973.

[37] (a) Langfredi, M. A.; Tiripiccio, A.; Natile, G.; Gasparrini, F.; Galli, B. *Cryst. Struct. Commun.* **1979**, *6*, 611. (b) Natile, G.; Gasparrini, F.; Missiti, D. M.; Perego, G. *J. Chem. Soc., Dalton Trans.* **1977**, 1747. (c) Katti, K. V.; Ge, Y. W.; Sing, P. R.; Date, S. V.; Barnes, C. L. *Organometallics* **1994**, *13*, 541. (d) Codina, G.; Caubet, A.; López, C.; Moreno, V.; Molins, E. *Helv. Chim. Acta* **1999**, *82*, 1025. (e) Pérez, S.; Bosque, R.; López, C.; Solans, X.; Font-Bardía, M. *J. Organomet. Chem.* **2001**, *625*, 67. (f) López, C.; Bosque, R.; Solans, X.; Font-Bardia, M. *Polyhedron* **2001**, *20*, 987.

for **4a**,**b**, **5b**, and **8b**, respectively), and they deviate by ca. −24.46° (in **4a**), 30.8° (in **4b**), 13.9° (in **5b**), or 11.46° (in **8b**) from the ideal eclipsed conformation. In all cases, the distance between the two metal atoms (4.5397 Å (in **4a**), 4.4954 Å (in **4b**), 4.5648 Å (in **5b**), and 5.2064 Å (in **8b**)) is clearly greater than the sum of the van der Waals radii of these atoms,[36] thus suggesting the absence of any direct interaction between the Fe and the Pd.



S = acetone,
x = 1 (**3a**) or 2 (**3b**)

x = 2 or 3 and
X = Cl or CH_3COO

Figure 5. Schematic view of (***A***) the structures proposed for the cationic arrays of the intermediate species **3** and (***B***) those of related dimeric cyclopalladated complexes derived from the ligands 4-$ClC_6H_4CH{=}NCH_2(CH_2)_xNMe_2$ (x = 1, 2) described recently, in which the mode of coordination of the ligands is similar to that proposed for compounds **3**.

Attempts To Clarify the Nature of the Intermediate Species 3. As a first approach to try to explain why a nearly invariant amount of compounds **2** was recovered after the treatment of these compounds with Tl[BF_4] (to give **3**) and the subsequent reaction with diphenylacetylene or hex-3-yne, we were prompted to attempt the characterization of these intermediate species **3**.[38] The infrared spectra of **3a**,**b** showed the typical bands due to the [BF_4]$^-$ anion,[17] but their proton NMR spectra were more complex than those initially expected for the monomeric derivatives [Pd{[(η^5-C_5H_3)-$CH{=}N(CH_2)_nNMe_2$]Fe(η^5-C_5H_5)}(acetone)][BF_4] (n = 2, 3), which arise from **2** by the abstraction of the Cl^- ligand and the subsequent coordination of the solvent (acetone). In fact, most of the signals observed in the ^{1}H NMR spectra of **3** appeared duplicated and none of them were coincident with those of the corresponding complex **2**. A similar feature was observed in the ^{13}C-{^{1}H} NMR spectra. These findings could be indicative that the intermediate species **3** could have higher nuclearity. Elemental analyses of these materials did not differ substantially from those expected for the polymeric complexes "{[Pd_2{[(η^5-C_5H_3)$CH{=}N(CH_2)_n$-NMe_2]Fe(η^5-C_5H_5)}$_2$Cl(acetone)][BF_4]}$_x$". The MALDI-TOF mass spectra showed a very intense signal at m/z 813 (for **3a**) and 842 (for **3b**), which are consistent with the values expected for the cations "[Pd_2{[(η^5-C_5H_3)$CH{=}N(CH_2)_nNMe_2$]Fe(η^5-C_5H_5)}$_2$Cl]$^+$" (n = 2, 3). Also, the values of the molar conductivity of 10^{-3} M solutions of **3** in acetone (128 (**3a**) and 140 Ω^{-1} cm^2 mol^{-1} (**3a**)) were in the upper range expected for a 1/1 electrolyte.[39] In the view of the characterization data available at this point, we tentatively postulate for the intermediate species **3** the dimeric structure [Pd_2{[(η^5-C_5H_3)$CH{=}N(CH_2)_nNMe_2$]Fe(η^5-C_5H_5)}$_2$Cl(acetone)][BF_4] (***A*** in Figure 5). Quite recently, some authors have reported the formation of the dimeric compounds [Pd{4-ClC_6H_4-$CH{=}N(CH_2)_nNMe_2$}X]$_2$ (***B*** in Figure 5) in the cyclopalladation of 4-$ClC_6H_4CH{=}N(CH_2)_nNMe_2$ (n = 2, 3).[40] These compounds can be visualized as derived from the parent ligands of **2**, [(η^5-C_5H_5)Fe{(η^5-C_5H_4)$CH{=}N(CH_2)_n$-

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[38] Characterization data for **3a** are as follows. Anal. Calcd for $C_{33}H_{44}ClBF_4Fe_2N_4OPd_2\cdot{}^1/_2H_2O$: C, 40.93; H, 4.74; N, 5.78. Found: C, 40.6; H, 4.8; N, 5.6. MS (MALDI-TOF$^+$) m/z 815 ([M − acetone − BF_4]$^+$). IR: 1583 cm^{-1} (ν(>C=N−)); 1705 cm^{-1} (br, ν(>CO)). ^{1}H NMR (in acetone-d_6): δ 4.35 and 4.33 (s, 10H, C_5H_5 and (C_5H_5)′); 4.46 and 4.50 (s, 2H, H^3 and $H^{3'}$); 4.65 and 4.70 (s, 2H, H^4 and $H^{4'}$); 4.87 and 4.90 (m, 2H, H^5 and $H^{5'}$); 8.03 and 8.07 (s, 2H, −CH=N− and (−CH=N−)′); 3.40−3.80 (m, 4H, =NCH_2− and (=NCH_2−)′); 2.90−3.10 (m, 4H, (−CH_2N−) and (−CH_2N−)′); 2.63 (s, 3H, Me); 2.64 (s, 3H, Me); 2.70 (s, 3H, Me); 2.84 (s, 3H, Me). ^{1}H NMR (in $CDCl_3$): δ 4.34 and 4.38 (s, 10H, C_5H_5 and (C_5H_5)′); 4.42 and 4.47 (s, 2H, H^3 and $H^{3'}$); 4.85 (br, 2H, H^4 and $H^{4'}$); 5.23 (br, 2H, H^5 and $H^{5'}$); 8.04 and 8.06 (s, 2H, −CH=N− and (−CH=N−)′); 3.35 and 3.50 (br m, 4H, =NCH_2− and (=NCH_2−)′); 2.60 (s, 6H, 2 Me); 2.66 (s, 3H, Me); 2.76 (s, 3H, Me); 2.47 (s, 3H, Me (acetone)); the signals due to the proton of the −CH_2N− unit were partially masked by those due to the methyl groups. ^{13}C-{^{1}H} NMR data (in $CDCl_3$): δ 70.7 and 70.2 (C_5H_5) and (C_5H_5)′); 92.3 and 92.7 (C^1 and $C^{1'}$); 100.2 and 100.7 (C^2 and $C^{2'}$); 75.90 and 68.96 (C^3 and $C^{3'}$); 65.9 and 66.6 (C^4 and $C^{4'}$); 67.5 (C^5); 173.1 and 174.0 (−CH=N− and (−CH=N−)′); 53.3 (br, =NCH_2− and (=NCH_2−)′); 63.60 and 63.89 −CH_2N and (−CH_2N)′); 48.0, 48.2 and 48.0 (Me and Me′); 30.9 (Me (acetone)) and 206.9 (>C(O), acetone). Characterization data for **3b** are as follows. Anal. Calcd for $C_{35}H_{48}ClBF_4Fe_2N_4OPd_2\cdot H_2O$: C, 41.81; H, 5.01; N, 5.57. Found: C, 41.7; H, 5.1; N, 5.8. MS (MALDI-TOF): m/z 842 ([M − acetone − BF_4]$^+$). IR: 1578 cm^{-1}. ^{1}H NMR (in acetone-d_6): δ 4.34 (s, 10H, C_5H_5 and (C_5H_5)′); 4.41 and 4.42 (s, 2H, H^3 and $H^{3'}$); 4.61 and 4.65 (s, 2H, H^4 and $H^{4'}$); 5.08 (m, 2H, H^5 and $H^{5'}$); 8.18 and 8.32 (s, 2H, −CH=N− and (−CH=N−)′); 3.18, 3.54, 3.36, and 3.18 (m, 4H, =NCH_2− and (=NCH_2−)′); 1.81 and 1.98 (m, 4H, −CH_2− and (−CH_2−)′); 2.60 and 2.83 (m, 4H, −CH_2N− and (−CH_2N−)′); 2.67, 2.04, 2.57, and 2.55 (4s, 12H, −NMe_2 and (−NMe_2)′). ^{1}H NMR (in $CDCl_3$): δ 4.33 and 4.40 (s, 10H, C_5H_5 and (C_5H_5)′), 4.45 and 4.30 (s, 2H, H^3 and $H^{3'}$); 4.42 and 4.56 (s, 2H, H^4 and $H^{4'}$); 5.30 (m, 2H, H^5 and $H^{5'}$); 8.07 and 8.11 (s, 2H, −CH=N− and (−CH=N−)′); 3.42 (br m, 4H, =NCH_2− and (=NCH_2−)′); 1.18, 1.30, 1.52, and 1.62 (m, 4H, −CH_2− and (−CH_2−)′); 2.30 and 2.70 (m, 4H, −CH_2N− and (−CH_2N−)′); 2.63 (s, 3H, Me); 2.67 (s, 6H, 2 Me); 2.72 (s, 3H, Me); 2.40 (s, 3H, Me (acetone)). ^{13}C{^{1}H} NMR data (in acetone-d_6): δ 70.4 (C_5H_5)and (C_5H_5)′), 80.9 and 85.5 (C^1 and $C^{1'}$); 99.9 and 100.1 (C^2 and $C^{2'}$); 74.0 and 68.8 (C^3 and $C^{3'}$); 67.4 and 74.7 (C^4 and $C^{4'}$); 70.4 (C^5), 175.1 and 176.6 (−CH=N− and (−CH=N−)′); 57.3 and 57.7 (=NCH_2− and (=NCH_2−)′); 26.4 and 26.5 (−CH_2− and (−CH_2−)′); 62.8 and 63.3 (−CH_2−N and (−CH_2−N)′); 48.1 and 48.9 (Me and Me′). ^{13}C{^{1}H} NMR (in $CDCl_3$): δ 71.3 and 71.6 (C_5H_5 and (C_5H_5)′), 86.4 and 86.7 (C^1 and $C^{1'}$); 96.8 and 104.1 (C^2 and $C^{2'}$); 77.5 (C^3 and $C^{3'}$); 67.6, 67.8, 69.4, and 69.6 (C^4, $C^{4'}$, C^5, and $C^{5'}$), 175.7 (br, −CH=N− and (−CH=N−)′); 63.1 and 63.8 (=NCH_2− and (=NCH_2−)′); 24.8 and 26.5 (−CH_2− and (−CH_2−)′); 57.9 and 59.8 (−CH_2N and (−CH_2N)′), 48.7, 49.2 (br) and 48.7 (Me and Me′; 29.9 (Me (acetone)); in this case the signal due to the carbon-13 nuclei of the >CO group of the acetone was not observed. For the two compounds the ^{1}H−^{1}H-NOESY experiments (in $CDCl_3$ at 20 °C) suggested that the halves of the cations of these compounds underwent a dynamic process in solution.

[39] Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 87.

[40] Gómez, M.; Granell, J.; Martinez, M. *Inorg. Chem. Commun.* **2002**, *5*, 67.

$NMe_2\}]$, by replacement of the ferrocenyl group by the 4-ClC_6H_4 moiety.

As mentioned above, in the insertion of the alkynes into the σ(Pd−C) bond of cyclopalladated complexes the first step involves the coordination of the alkyne in the cis arrangement to the metalated carbon.[16] For the structures proposed for **3**, the halves of the cations (hereinafter referred to as **I** and **II**) are not identical. In one of them (fragment **I**) the palladium(II) is bound to an acetone molecule, while in the other half of the cation (**II**) a chlorine is in a position cis to the metalated carbon. Since it is widely accepted that the Pd−O-(acetone) bond is more labile than the Pd−Cl bond,[41] the coordination of the alkyne is expected to be more likely to occur in fragment **I** than in the other half of the cation, where the palladium(II) is bound to a chlorine ligand. The results presented above revealed that compounds **2** (in which the chlorine and the metalated carbon are also in adjacent positions) did not react with the less reactive alkynes used in this work (diphenylacetylene and hex-3-yne).[18] Thus in these cases, only one fragment of the cation (half **I**) will allow the coordination of these alkynes and their subsequent insertion to produce the ionic compounds **4** and **5**. In contrast with these results, when the reaction was carried out with $Me_2OCC{\equiv}CCO_2Me$, which is more reactive, the halves of the molecule would be involved in the process: fragment **I** could lead to compounds **6** (which have a similar backbone to those of **4** and **5**), while the other half would produce the neutral derivatives $[Pd\{[(MeO_2CC{=}CCO_2Me)(\eta^5\text{-}C_5H_3)CH{=}N(CH_2)_nNMe_2]Fe(\eta^5\text{-}C_5H_5)\}Cl]$ (n = 2 (**7a**), 3 (**7b**)), which are also formed in the reaction of compounds **2** with $Me_2OCC{\equiv}CCO_2Me$ in the absence of Tl(I) salts.

Conclusions

The results reported here reveal that the compounds $[Pd\{[(\eta^5\text{-}C_5H_3)CH{=}N(CH_2)_nNMe_2]Fe(\eta^5\text{-}C_5H_5)\}Cl]$ (n = 2 (**2a**), 3 (**2b**)) are less prone to undergo the bis insertion of diphenylacetylene or hex-3-yne than the corresponding dimeric derivatives $[Pd\{[(\eta^5\text{-}C_5H_3)C(R^2){=}NR^3]Fe(\eta^5\text{-}C_5H_5)\}(\mu\text{-}Cl)]_2$ (**1**).[12] This finding may be due to several causes, among which the mode of binding of the ligand and/or the strength of the Pd−Cl bonds appear to be the most relevant. On the other hand, since the intermediate species formed by the addition of thallium(I) salts (**3a**,**b**) are more reactive than the starting materials **2a**,**b**, the proclivity of the three sorts of cyclopalladated derivatives to undergo insertion of the alkynes increases according to the sequence: **2a** < **2b** < **3a** < **3b** < **1**. This trend shows that tiny changes in the $[C(sp^2,\text{ferrocene}),N,N']^-$ terdentate ligand, such as the incorporation of a $-CH_2-$ moiety in the chelate ring, play also a crucial role in the tuning of the reactivity of these sorts of compounds with the alkynes studied. In addition, since for palladacycles containing $[C(sp^2,\text{phenyl}),N]^-$ bidentate ligands it has been demonstrated that the first step of the insertion process requires the binding of the alkyne to the metal in the position adjacent to the σ(Pd−C) bond,[16] the differences observed in the reactivity of compounds **1**−**3** could be related to the different labilities of the bonds between the palladium(II) and the ligands on a arrangement cis to the metalated carbon. On the other hand, the variations detected in the σ(M−ligand) bond lengths within a family of related complexes has been frequently used to rationalize the different reactivities of these compounds toward a given ligand. Commonly, for a given ligand (L), larger σ(M−ligand) bond distances are related to the greater lability of the bond. However, the comparison of structural data of compounds **2a**,**b** presented in Table 6 show that, despite the fact that the results presented in this work provide conclusive evidence of the higher reactivity of complex **2b** versus the alkyne $MeO_2CC{\equiv}CCO_2Me$, when compared with that of **2a**, the Pd−Cl bond length is (2.3143(9) Å) shorter, if significant, than in **2a** (2.328(3) Å[25]), and in the two cases the Pd−C bond lengths involved in the insertion process are practically identical: (1.963(7) Å in **2a** and 1.964(3) Å in **2b**); thus, these findings suggest that other more subtle factors, i.e. the accessibility of the alkyne to the metal center, the steric effects induced by the chelate ring, or its flexibility, may also play an important role in these sorts of processes.

Table 6. Selected Bond Lengths (in Å) and Bond Angles (in deg) around the Palladium Atom in $[Pd\{[(\eta^5\text{-}C_5H_3)CH{=}N(CH_2)_nNMe_2]Fe(\eta^5\text{-}C_5H_5)\}Cl]$ (n = 2 (2a),[25] 3 (2b)[13])[a]

	2a	2b
Pd−Cl	2.328(3)	2.3143(9)
Pd−C	1.963(7)	1.964(3)
Pd−N(1)	1.960(6)	2.052(3)
Pd−N(2)	2.196(4)	2.205(3)
C−Pd−Cl	96.1(2)	91.27(10)
Cl−Pd−N(2)	100.40(14)	92.86(8)
N(1)−Pd−C	80.5(3)	81.02(12)
N(2)−Pd−N(1)	82.59(18)	94.56(11)

[a] N(1) and N(2) represent the imine and amine nitrogen atoms, respectively, and C indicates the metalated carbon atom. Standard deviation parameters are given in parentheses.

In addition, the results obtained from these studies indicate that the nature of the substituents, R^1, on the alkyne plays a crucial role in the determining the size of the metallacycle formed by the insertion. For the alkynes holding electron-donor groups the formation of the ionic compounds $[Pd\{[(R^1C{=}CR^1)_2(\eta^5\text{-}C_5H_3)CH{=}N(CH_2)_nNMe_2]Fe(\eta^5\text{-}C_5H_5)\}][BF_4]$ (n = 2, 3 and R^1 = Ph, Et) through a bis insertion process is strongly preferred, while if the reaction was performed under identical conditions but using $MeO_2CC{\equiv}CCO_2Me$, which contains an electron-withdrawing substituent, in addition to the compounds $[Pd\{[(MeO_2CC{=}CCO_2Me)_2(\eta^5\text{-}C_5H_3)CH{=}N(CH_2)_nNMe_2]Fe(\eta^5\text{-}C_5H_5)\}][BF_4]$ (**6**), the monoinsertion derivatives $[Pd\{[(MeO_2CC{=}CCO_2Me)(\eta^5\text{-}C_5H_3)CH{=}N\text{-}(CH_2)_nNMe_2]Fe(\eta^5\text{-}C_5H_5)\}Cl]$ (**7**; n = 2, 3) were also obtained.

The study of the reactions of compounds **2** with the alkynes $R^1C{\equiv}CR^1$ has allowed the obtainment of a wide variety of neutral and ionic palladacycles containing seven- or nine-membered rings, and since it is well-known that the applications of cyclopalladated complexes as precursors for organic or organometallic synthesis are commonly based on their reactions with alkynes, followed by depalladation processes, compounds **3**−**8** presented here appear to be excellent

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[41] *Comprehensive Organometallic Chemistry: The Synthesis, Reactions and Structure of Organometallic Compounds*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1982; Vol. 6, p 236.

substrates for clarifying the influence of the size of the chelate ring upon the nature of the final depalladation products. Studies in this field are currently under way.

Experimental Section

General Comments. The alkynes R^{1}C≡CR^1 (with R^1 = Ph, Et, CO$_2$Me) were obtained from commercial sources and used as received. The palladium(II) complexes [Pd{[(η^5-C$_5$H$_3$)CH=N(CH$_2$)$_n$NMe$_2$]Fe(η^5-C$_5$H$_5$)}Cl] (n = 2 (**2a**), 3 (**2b**)) were prepared as described previously.[13,14] Some of the preparations described below require the use of *hazardous materials* such as Tl[BF$_4$], which should be handled with *caution*. Tl[BF$_4$] was prepared as reported previously.[42] The solvents used were dried and distilled according to the procedures described in the literature.[43]

Elemental analyses were carried out at the Serveis Cientifico-Tècnics (Universitat de Barcelona), at the Serveis de Recursos Cientifics i Tècnics (Universitat Rovira Virgili, Tarragona, Spain), or at the Institut de Quimica Bio-Orgànica, (CSIC, Barcelona, Spain). Infrared spectra were obtained with a Nicolet-500FTIR instrument using KBr pellets. Routine ^{1}H NMR spectra were recorded at ca. 20 °C on a Gemini-200 MHz instrument using CDCl$_3$ (99.9%) as solvent and SiMe$_4$ as internal standard, except for compounds **3**, for which the solvent used for the NMR studies was acetone-d_6 (99.9%). High-resolution ^{1}H NMR and the two-dimensional {^{1}H-^{1}H} NOESY and the {^{1}H−^{13}C} heteronuclear correlation experiments (HMBC and HSQC) were recorded with either a Varian VRX-500 or a Bruker Advance DMX-500 instrument. ^{13}C{^{1}H} NMR spectra were obtained with a Mercury-400 instrument. Mass spectra (MALDI-TOF$^+$ for compounds **3** and FAB$^+$ for the remaining complexes) were registered at the Servei de Espectrometría de Masses (Universitat de Barcelona) with VOYAGER-DE-RP and VG-Quatro instruments, respectively. For the FAB$^+$ spectra, nitrobenzyl alcohol (NBA) was used as matrix; for MALDI-TOF$^+$, 2-hydroxybenzoic acid (DHB) was used as matrix. Molar conductivity measurements of 10^{-3} M solutions of **3** in acetone were determined at 20 °C with a CRISON conductivity meter.

Preparation of [Pd{[(PhC=CPh)$_2$(η^5-C$_5$H$_3$)CH=N(CH$_2$)$_2$-NMe$_2$]Fe(η^5-C$_5$H$_5$)}][BF$_4$]·CH$_2$Cl$_2$ (4a). A 114 mg (3.9 × 10^{-4} mol) amount of Tl[BF$_4$] was added to a solution formed by 111 mg (2.6 × 10^{-4} mol) of **2a** and 20 mL of acetone. The reaction mixture was stirred at room temperature (ca. 20 °C) for 2 h. After this period the undissolved materials were removed by filtration and discarded. The red-brown filtrate was concentrated to dryness on a rotary evaporator, and the gummy residue obtained was then treated with 15 mL of CH$_2$Cl$_2$ and filtered out. Then, diphenylacetylene (93 mg, 5.2 × 10^{-4} mol) was added to the filtrate and the reaction mixture was refluxed for 2 h. After this period the resulting solution was concentrated to ca. 5 mL on a rotary evaporator and was passed through a small SiO$_2$ chromatography column (4.5 cm × 2 cm). Elution with CH$_2$Cl$_2$ produced the release of a red band, which led after concentration to dryness to small amounts (40 mg) of the starting material. The subsequent elution with a CH$_2$Cl$_2$/MeOH (100/1) solution produced the release of an orange band, which was collected and concentrated to dryness on a rotary evaporator, giving **4a** as an orange-brown solid (yield 82 mg, 34%). Characterization data are as follows. Anal. Calcd for C$_{43}$H$_{39}$BF$_4$FeN$_2$Pd·CH$_2$Cl$_2$: C, 57.58; H, 4.54; N, 2.95. Found: C, 58.08; H, 4.65; N, 3.01. MS (FAB$^+$): *m*/*z* 758.8 ([M] − Cl − BF$_4$)}$^+$. IR: 1637 cm^{-1} (ν(>C=N−)). ^{1}H NMR:[44] δ 4.33 (s, 5H, C$_5$H$_5$); 4.71 (s, 1H, H^3); 4.76 (s, 1H, H^4); 4.80 (s, 1H, H^5); 8.25 (s, 1H, −CH=N−); 3.54 and 3.95 (m, 2H, =NCH$_2$−), 2.76 and 3.08 (m, 2H, −CH$_2$N); 2.55 (s, 3H, Me); 2.40 (s, 3H, Me); 6.35−7.60 (m, 20 H, Ph); 5.12 (s, 2H, CH$_2$Cl$_2$). ^{13}C{^{1}H} NMR data (selected data):[44] δ 72.8 (C$_5$H$_5$); 88.2 (C^1); 70.8 (C^2); 77.1 (C^3); 74.5 (C^4); 74.1 (C^5); 166.3 (−CH=N−); 66.5 (=NCH$_2$−); 55.9 (−CH$_2$N−), 50.6 (Me) and 49.4 (Me); 94.76, 114.0, 144.6, and 145.9 (C$^\alpha$, C$^\beta$, C$^\delta$, and C$^\gamma$).

Preparation of [Pd{[(PhC=CPh)$_2$(η^5-C$_5$H$_3$)CH=N(CH$_2$)$_3$-NMe$_2$]Fe(η^5-C$_5$H$_5$)][BF$_4$]·CH$_2$Cl$_2$ (4b). An acetone solution (20 mL) containing 210 mg (4.58 × 10^{-4} mol) of **2b** was treated with Tl[BF$_4$] (199 mg, 6.83 × 10^{-4} mol), and the resulting mixture was stirred for 3 h at room temperature. The solid formed during this period, TlCl, was removed by filtration, and the filtrate was concentrated to dryness on a rotary evaporator. The residue was then treated with CH$_2$Cl$_2$ (ca. 20 mL) and filtered out to remove the unreacted Tl[BF$_4$]. Then PhC≡CPh (163 mg, 9.14 × 10^{-4} mol) was added to the filtrate and the reaction mixture was refluxed for 2 h. The resulting solution was filtered out, and the filtrate was concentrated to dryness on a rotary evaporator. The residue was then passed through a SiO$_2$ column (4.5 cm × 2 cm). Elution with CH$_2$Cl$_2$ produced the release of a red band containing the unreacted **2b** (54 mg). Once this band was collected, a CH$_2$Cl$_2$/MeOH (100/1) mixture eluted an orange band which gave, after concentration to dryness, compound **4b** (99 mg, 23%). Characterization data are as follows. Anal. Calcd for C$_{44}$H$_{41}$N$_2$BF$_4$FePd·$^3/_4$CH$_2$Cl$_2$: C, 59.03, H, 4.79; N, 3.08. Found: C, 59.0; H, 4.8; N, 3.2. MS (FAB$^+$): *m*/*z* 759 ([M − BF$_4$]$^+$). IR: 1637 cm^{-1} (ν(>C=N−)). ^{1}H NMR:[43] δ 4.31 (s, 5H, C$_5$H$_5$); 4.52 (s, 1H, H^3); 4.74 (s, 1H, H^4), 4.77 (s, 1H, H^5); 7.94 (s, 1H, −CH=N−); 3.62 and 3.70 (m, 2H, =NCH$_2$−); 2.08 and 2.18 (m, 2H, −CH$_2$−); 2.69 and 3.20 (m, 2H, −CH$_2$N−); 2.56 (s, 3H, Me); 2.41 (s, 3H, Me); 6.40−7.35 (m, 20H, aromatic); 5.12 (s, 2H, CH$_2$Cl$_2$). ^{13}C{^{1}H} NMR selected data:[43] δ 72.1 (C$_5$H$_5$); 88.3 (C^1); 71.9 (C^2); 76.6 (C^3); 72.9 (C^4); 74.1 (C^5); 168.4 (−CH=N−); 54.7 (=N−CH$_2$−); 23.5 (−CH$_2$−); 60.4 (−CH$_2$−N); 52.6 (Me); 47.6 (Me).

Preparation of [Pd{[(EtC=CEt)$_2$(η^5-C$_5$H$_3$)CH=N-(CH$_2$)$_2$NMe$_2$]Fe(η^5-C$_5$H$_5$)][BF$_4$]·CH$_2$Cl$_2$ (5a). This compound was prepared by following the same procedure as described for **4a**, but using 150 mg (3.5 × 10^{-4} mol) of **2a**, 154 mg (5.3 × 10^{-4} mol) of Tl[BF$_4$], and hex-3-yne (0.85 mL, 7.5 × 10^{-4} mol) as starting materials. In this case the reaction mixture was refluxed for 6 h, and the workup of the column led to unreacted **3** (60 mg) and a gummy material which was dried under reduced pressure for 5 days, giving the bright orange solid **5a** (73 mg, 25%). Characterization data for **5a** are as follows. Anal. Calcd for C$_{27}$H$_{39}$BF$_4$FeN$_2$Pd·CH$_2$Cl$_2$: C, 50.71; H, 4.50; N, 4.25. Found: C, 50.62; H, 4.37; N, 4.14. MS (FAB$^+$): *m*/*z* 553 ([M − BF$_4$]$^+$). IR: 1632 cm^{-1} (ν(>C=N−)).^{1}H NMR:[44] δ 4.34 (s, 5H, C$_5$H$_5$); 4.60 (s, 2H, H^3 and H^4); 4.77 (s, 1H, H^5); 8.32 (s, 1H, −CH=N−); 3.60−3.68 (br m, 2H, =NCH$_2$−); 2.80−2.98 (br m, 2H, −CH$_2$N); 2.85 (s, 3H, Me); 2.69 (s, 3H, Me); 1.50, 2.15, 2.77, and 2.62 (br m, 8H, 4 −CH$_2$− (Et)) and four triplets at 1.54, 1.09, 0.94, and 0.89 due to the protons of the −CH$_3$ fragment of the four ethyl groups. ^{13}C{^{1}H} NMR data:[44] δ 70.2 (C$_5$H$_5$); 86.9 (C^1); 70.1 (C^2); 70.8 and 71.2 (C^3 and C^4); 72.4 (C^5); 165.7 (−CH=N−); 69.3 (=NCH$_2$−); 64.7 (−CH$_2$N); 49.1 (Me) and 50.4 (Me); 20.1, 21.4, 24.3, 34.2 (−CH$_2$ (Et)); 11.39, 13.7, 14.4, and 17.1 (−CH$_3$ (Et)); and four signals at 103.7, 110.3, 139.8, and 141.0 due to the four quaternary carbon nuclei (C$^\alpha$, C$^\beta$, C$^\delta$, and C$^\gamma$, respectively) of the inserted η^3-butadienyl moiety.

Preparation of [Pd{[(EtC=CEt)$_2$(η^5-C$_5$H$_3$)CH=N(CH$_2$)$_3$-NMe$_2$]Fe(η^5-C$_5$H$_5$)}][BF$_4$]·CH$_2$Cl$_2$ (5b). This compound was prepared according to the procedure described for **5a**, but using 193 mg (4.39 × 10^{-4} mol) of **2b**, 192 mg (6.59 × 10^{-4} mol) of Tl[BF$_4$], and 0.100 mL (8.80 × 10^{-4} mol) of hex-3-yne, and in this case the reaction mixture was refluxed for 2 h. Elution with CH$_2$Cl$_2$ produced compound **2b**, and subsequent elution with CH$_2$Cl$_2$/MeOH (100/1) produced the release of an orange band that led after concentration to a gummy red residue,

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[42] Kowala, C.; Swan, J. M. *Aust. J. Chem*. **1966**, *19*, 547.

[43] Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon Press: London, 1998.

[44] Labeling of the atoms corresponds to those shown in the schemes and charts.

which was dried under vacuum for 3 days, giving **5b** as a bright orange solid (yield 53 mg, 18%). Good-quality crystals of **5b** suitable for X-ray study were isolated by slow evaporation of a CH_2Cl_2 solution of the solid sample layered with *n*-hexane. Characterization data for **5b** are as follows. Anal. Calcd for $C_{28}H_{41}BF_4FeN_2Pd\cdot{}^1/_2H_2O$: C, 50.67; H, 6.37; N, 4.22. Found: C, 50.5; H, 6.7; N, 4.2. MS (FAB$^+$): *m/z* 567 ([M − BF_4]$^+$). IR: 1637 cm^{-1} (ν(>C=N−)).^{1}H NMR:[44] δ 4.38 (s, 5H, C_5H_5); 4.65 (s, 2H, H^3 and H^4); 4.87 (s, 1H, H^5); 8.39 (s, 1H, −CH=N−), 3.84 (m, 2H, =NCH$_2$−); 2.75−3.02 (m, 10H, 2Me, −CH$_2$N and 1 −CH$_2$− (Et)); 2.14−2.24 (m, 6H, −CH$_2$− and 2 −CH$_2$− (Et)); 1.50 (m, 2H, −CH$_2$− (Et)); and four triplets at 0.94, 0.97, 1.13, and 1.62 due to the protons of the −CH$_3$ fragment of the four ethyl groups. $^{13}C\{^1H\}$ NMR:[44,45] δ 71.5 (C_5H_5); 87.9 (C^1); 70.4 and 71.6 (C^3 and C^4); 73.2 (C^5); 168.9 (−CH=N−); 55.3 (=NCH$_2$− and Me); 60.8 (−CH$_2$N); 36.2, 24.3, and 22.3 (−CH$_2$− and CH$_2$ (Et)); 12.9, 13.7, 15.2, and 19.2 (−CH$_3$ (Et)); and four signals at 97.9, 116.1, 142.8, and 143.1 due to the four quaternary carbon nuclei (C^α, C^β, C^δ, and C^γ, respectively, of the inserted η^3-butadienyl moiety).

Preparation of [Pd{[(MeO$_2$CC=CCO$_2$Me)$_2$(η^5-C$_5$H$_3$)CH=N(CH$_2$)$_2$NMe$_2$]Fe(η^5-C$_5$H$_5$)}][BF$_4$] (6a). This compound was prepared as described above for **4a** but using **2a** (140 mg, 3.3 × 10^{-4} mol), Tl[BF$_4$] (143 mg, 4.9 × 10^{-4} mol), and MeO$_2$CC≡CCO$_2$Me (0.81 mL, 6.6 × 10^{-4} mol). In this case once the refluxing period finished, the solution was filtered out and the filtrate was concentrated to ca. 10 mL on a rotary evaporator. Addition of *n*-hexane to the resulting solution produced the precipitation of **6a** as a red-purple solid, which was filtered out, washed with small portions (ca. 2 mL) of *n*-hexane, air-dried, and then dried under vacuum (yield 101 mg, 25%). The slow evaporation of the yellow filtrate produced compound **7a** (yield 52 mg). Characterization data for **6a** are as follows. Anal. Calcd for $C_{28}H_{33}BF_4FeN_2O_8Pd\cdot{}^1/_2CH_2Cl_2$: C, 41.13; H, 4.02; N, 3.49. Found: C, 40.92; H, 4.11; N, 3.49. MS (FAB$^+$): *m/z* 673 ([M − (BF$_4$)]$^+$). IR: 1635 cm^{-1} (ν(>C=N−)); 1710 and 1692 cm^{-1} ((br), ν(>COO)). ^{1}H NMR:[44] δ 4.47 (s, 5H, C_5H_5); 4.90 (s, 1H, H^3); 4.96 (s, 1H, H^4); 5.22 (s, 1H, H^5); 8.05 (s, 1H, −CH=N−); 3.94 and 4.05 (m, 2H, =NCH$_2$−); 2.80 and 3.20 (m, 2H, −CH$_2$N); 3.02 (s, 3H, Me); 2.99 (s, 3H, Me); four singlets at 3.61, 3.76, 3.90, and 3.97 (12H, 4 OMe) and 5.12 (s, 1H, CH_2Cl_2). $^{13}C\{^1H\}$ NMR:[44,45] δ 71.8 (C_5H_5); 88.1 (C^1); 75.1 (C^3); 74.6 (C^4); 77.2 (C^5); 168.1 (−CH=N−); 65.7 (=NCH$_2$−); 57.2 (−CH$_2$N−); 48.6 (Me); 50.4 (Me); 52.8, 52.6, 51.8, and 51.5 (4 OMe); 159.2, 164.7, 167.2, and 169.5 (4 −COO); and four additional signals at 112.1, 136.2, 137.0, and 150.0 assigned to C^α, C^β, C^δ, and C^γ of the inserted η^3-butadienyl moiety.

Preparation of [Pd{[(MeO$_2$CC=CCO$_2$Me)$_2$(η^5-C$_5$H$_3$)CH=N(CH$_2$)$_3$NMe$_2$]Fe(η^5-C$_5$H$_5$)}][BF$_4$] (6b) and [Pd{[(MeO$_2$CC=CCO$_2$Me)$_2$(η^5-C$_5$H$_3$)CH=N(CH$_2$)$_3$NMe$_2$]Fe(η^5-C$_5$H$_5$)}Cl] (8b). Compound **2b** (269 mg, 6.13 × 10^{-4} mol) was dissolved in 20 mL of acetone, and then 266 mg (9.13 × 10^{-4} mol) of Tl[BF$_4$] was added. The reaction mixture was stirred at room temperature for 2 h and then filtered out to remove the thallium(I) chloride formed. The filtrate was concentrated to dryness on a rotary evaporator, and the residue was treated with CH_2Cl_2. The undissolved materials (TlCl and the unreacted Tl[BF$_4$]) were removed by filtration. Then the alkyne MeO$_2$CC≡CCO$_2$Me (0.150 mL, 1.22 ×10^{-4} mol) was added slowly and the reaction mixture was refluxed for 2 h. After this period, the solution was filtered out and the filtrate was concentrated to dryness on a rotary evaporator, giving a deep red solid, which was dissolved in the minimum amount of CH_2Cl_2 and passed through a SiO_2 chromatography column (4.5 cm × 2 cm) using a CH_2Cl_2/MeOH (100/1) mixture as eluant. The first yellow band collected was concentrated to dryness, giving 80 mg of [Pd{[(MeO$_2$CC=CCO$_2$Me)(η^5-C$_5$H$_3$)CH=N(CH$_2$)$_3$NMe$_2$]Fe(η^5-C$_5$H$_5$)}Cl] (**7b**), which arises from the monoinsertion of the alkyne. A small amount (15 mg) of [Pd{[(MeO$_2$CC=CCO$_2$Me)$_2$(η^5-C$_5$H$_3$)CH=N(CH$_2$)$_3$NMe$_2$]Fe(η^5-C$_5$H$_5$)}Cl] (**8b**) was isolated from the second yellow band released from the column. Once this band was collected, the elution with CH_2Cl_2/MeOH (100/1.5) produced the release of a deep purple band containing compound **6b**, which was isolated as a solid by concentration to dryness on a rotary evaporator (yield 40 mg, 8%). Characterization data for **6b** are as follows. MS (FAB$^+$): *m/z* 688 ([M − (BF$_4$)]$^+$). IR: 1635 cm^{-1} (ν(>C=N−)) and 1728 cm^{-1} (br, ν(>COO)). ^{1}H NMR:[44] δ 4.52 (s, 5H, C_5H_5); 4.94 (s, 1H, H^3); 5.09 (s, 1H, H^4); 5.16 (s, 1H, H^5); 8.56 (s, 1H, −CH=N−); 3.67 and 3.94 (m, 2H, =NCH$_2$−); 2.20 and 2.54 (m, 2H, −CH$_2$−); 2.88 and 3.12 (m, 2H, −CH$_2$N−); 3.05 (s, 3H, Me); 2.82 (s, 3H, Me); and four singlets at 3.60, 3.72, 3.87, and 3.96 (s, 12H, 4 OMe). $^{13}C\{^1H\}$ NMR:[44] δ 73.2 (C_5H_5); 77.7 (C^1); 70.5 (C^2); 75.9 (C^3); 74.6 (C^4); 76.9 (C^5); 171.9 (−CH=N−); 54.7 (=NCH$_2$−); 23.7 (−CH$_2$−); 61.0 (−CH$_2$N−); 54.4 (Me); 50.2 (Me); 52.7, 53.1, 53.6, and 54.1 (4 OMe); 158.8, 163.1, 166.6, and 168.2 (4 −COO); and three additional signals at 118.9 (C^α), 135.1 (C^β and C^δ), 149.7 (C^γ) of the inserted η^3-butadienyl moiety. Characterization data for **8b** are as follows. Anal. Calcd for $C_{28}H_{33}FeClN_2O_8Pd\cdot CH_2Cl_2$: C, 43.10; H, 4.36 and N, 3.50. Found: C, 43.7; H, 4.6; N, 3.5. MS (FAB$^+$): *m/z* 688 ([M − Cl]$^+$). IR: 1624 cm^{-1} (ν(>C=N−)); 1734, 1724, 1714, and 1698 cm^{-1} (ν(>COO)). ^{1}H NMR:[44] δ 4.24 (s, 5H, C_5H_5); 4.57 (d, 1H, H^3, ^3J(H−H) = 2.5 Hz); 4.61 (t, 1H, H^4, ^3J(H−H) = 2.5 Hz); 4.80 (d, 1H, H^5, ^3J(H−H) = 2.5 Hz); 7.96 (s, 1H, −CH=N−); 3.69 and 4.70 (m, 2H, =NCH$_2$−); 1.77 and 2.10 (m, 2H, −CH$_2$−); 2.67 and 2.80 (m, 2H, −CH$_2$N−); 2.76 (s, 3H, Me); 2.45 (s, 3H, Me); and four singlets at 3.69, 3.75, 3.77, and 4.07 (s, 12H, 4 OMe). $^{13}C\{^1H\}$ NMR:[44] δ 71.5 (C_5H_5); 80.4 (C^1); 71.7 (C^2); 77.8 (C^3); 72.7 (C^4); 76.7 (C^5); 169.2 (−CH=N−); 62.1 (=NCH$_2$−); 26.3 (−CH$_2$−); 58.3 (−CH$_2$N−); 49.5 (Me); 47.8 (Me); 51.5, 52.1, 52.5, and 52.6 (4 −OMe); 163.2, 165.5, 169.0, and 171.8 (4 −COO); and four additional signals at 125.4, 138.3, 139.9, and 158.8, assigned to C^α, C^β, C^δ, and C^γ of the inserted η^3-butadienyl moiety.

Preparation of [Pd{[(MeO$_2$CC=CCO$_2$Me)(η^5-C$_5$H$_3$)CH=N(CH$_2$)$_n$NMe$_2$]Fe(η^5-C$_5$H$_5$)}Cl] (n = 2 (7a), 3 (7b)). Although these compounds were also isolated as byproducts during the synthesis of **6a** or **6b**, the procedure described here allows their isolation in a higher yield. The corresponding complex (**2a**,**b**; 4.08 × 10^{-4} mol) was dissolved in CH_2Cl_2 (ca. 5 mL), and then an equimolar amount of MeO$_2$CC≡CCO$_2$Me (0.050 mL, 4.08 × 10^{-4} mol) was added. The reaction mixture was refluxed for 21 h (for **7a**) or for 6 h (for **7b**) and then filtered out. The undissolved materials were discarded, and the filtrate was concentrated to dryness on a rotary evaporator. The residue was then dissolved in the minimum amount of CH_2Cl_2 and passed through a SiO_2 column (4 cm × 2 cm) using a CH_2Cl_2/MeOH (100/1) mixture as eluant. The yellow band that was released was collected and concentrated to dryness on a rotary evaporator (yield 118 mg (70.6%) for **7a** and 98 mg (42%) for **7b**). Characterization data for **7a** are as follows. Anal. Calcd for $C_{21}H_{25}FeClN_2O_4Pd\cdot CH_2Cl_2$: C, 40.52; H, 4.17; N, 4.30. Found: C, 40.9; H, 4.2; N, 4.4. MS (FAB$^+$): *m/z* 531 ([M − Cl]$^+$). IR: 1646 cm^{-1} (ν(>C=N−)) and 1716 cm^{-1} (ν(>COO)).^{1}H NMR:[44] δ 4.20 (s, 5H, C_5H_5); 4.54 (t, 2H, H^3); 4.58 (t, 1H, H^4, ^3J(H−H) = 2.5 Hz); 5.39 (t, 1H, H^5, ^3J(H−H) = 2.5 Hz); 8.21 (s, 1H, −CH=N−); 3.54 and 4.08 (m, 2H, =NCH$_2$−); 2.38 and 2.40 (m, 2H, −CH$_2$N); 2.81 (s, 3H, Me); 2.51 (s, 3H, Me); 3.73 and 3.71 (s, 6H, 2 −OMe); 5.25 (s, 2H, CH_2Cl_2). $^{13}C\{^1H\}$ NMR:[44] δ 70.9 (C_5H_5), 79.9 (C^1); 72.4 (C^2); 73.0 (C^3); 75.0 (C^4); 76.4 (C^5); 169.6 (−CH=N−); 64.9 (=NCH$_2$−); 62.1 (−CH$_2$N−); 50.0 (Me); 47.7 (Me); 51.4 and 51.7 (2 OMe); 174.2 and 165.7 (2 −COO), 133.4 and 139.1 (C^α and C^β of the inserted η^2-alkene). Characterization data for **7b** are as follows. Anal. Calcd for $C_{22}H_{27}FeClN_2O_4Pd\cdot{}^1/_2CH_2Cl_2$: C, 43.33; H, 4.52; N, 4.49. Found: C, 43.0; H, 4.5; N, 4.4. MS (FAB$^+$): *m/z* 545 ([M − Cl]$^+$). IR: 1635 cm^{-1} (ν(>C=N−)), 1715 and 1693 cm^{-1} (ν(>COO)). ^{1}H NMR:[44] δ 4.17 (s, 5H, C_5H_5); 4.59 (s, 1H, H^3); 4.63 (t, 1H, H^4); 5.27 (t, 1H, H^5, ^3J(H−H) = 2.5 Hz); 8.29 (s,

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(45) In this case, the signal due to the C^2 nuclei was not observed.

Table 7. Crystal Data and Details of the Refinement of the Crystal Structures of $[Pd\{[(PhC{=}CPh)_2(\eta^5\text{-}C_5H_3)CH{=}N(CH_2)_nNMe_2]Fe(\eta^5\text{-}C_5H_5)\}][BF_4]\cdot CH_2Cl_2$ (n = 2 (4a), 3 (4b)), $[Pd\{[(EtC{=}CEt)_2(\eta^5\text{-}C_5H_3)CH{=}N(CH_2)_3NMe_2]Fe(\eta^5\text{-}C_5H_5)\}][BF_4]\cdot CH_2Cl_2$ (5b), and $[Pd\{[(MeO_2CC{=}CCO_2Me)_2(\eta^5\text{-}C_5H_3)CH{=}N(CH_2)_3NMe_2]Fe(\eta^5\text{-}C_5H_5)\}Cl]\cdot CH_2Cl_2$ (8b)

	4a	**4b**	**5b**	**8b**
empirical formula	$C_{43}H_{39}N_2FePdBF_4\cdot CH_2Cl_2$	$C_{44}H_{43}N_2FePdBF_4\cdot CH_2Cl_2$	$C_{28}H_{41}N_2FePdBF_4$	$C_{29}H_{35}Cl_3FeN_2O_8Pd$
mol wt	917.75	932.78	654.69	808.19
T (K)	293(2)	293(2)	293(2)	293(2)
λ (Å)	0.710 69	0.710 69	0.710 69	0.710 69
cryst size (mm)	0.1 × 0.1× 0.2	0.1 × 0.1× 0.2	0.1 × 0.1× 0.2	0.1 × 0.1× 0.2
cryst syst	rhombic	monoclinic	orthorhombic	monoclinic
space group	$Pc2_1b$	$P2_1/c$	$Pc2_1/n$	$P2_1/n$
a (Å)	10.036(1)	20.528(1)	12.109(1)	13.757(1)
b (Å)	18.672(1)	9.635(1)	14.665(1)	14.324(1)
c (Å)	21.422(1)	21.695(1)	16.270(1)	16.958(1)
$\alpha = \gamma$ (deg)	90.0	90.0	90.0	90.0
β (deg)	90.0	103.385(1)	90.0	90.941(1)
V (Å^3)	4014.3(5)	4172.5(5)	2889.2(4)	3341.2(4)
Z	4	4	4	4
D_{calcd} (Mg m^{-3})	1.519	1.485	1.505	1.607
μ (mm^{-1})	0.995	0.959	1.170	1.262
F(000)	1864	1900	1344	1640
θ range for data collecn (deg)	1.90−28.83	2.86−28.38	3.02−31.11	1.89−31.65
no. of collected rflns	19 243	10 604	13 452	13 816
no. of unique rflns (R_{int})	4526 (0.0390)	4666 (0.0367)	3606 (0.0342)	8578 (0.0475)
no. of params	523	598	335	427
goodness of fit	0.854	1.000	1.062	1.048
refinement method	full-matrix least-squares on F^2			
R indices ($I > 2\sigma$(I))	R1 = 0.0395, wR2 = 0.0894	R1 = 0.0302, wR2 = 0.0751	R1 = 0.0389, wR2 = 0.0900	R1 = 0.0345, wR2 = 0.0836
R indices (all data)	R1 = 0.1386, wR2 = 0.1021	R1 = 0.0536, wR2 = 0.0807	R1 = 0.0498, wR2 = 0.0950	R1 = 0.0746, wR2 = 0.0909
abs structure param	0.04(3)		0.06(4)	
largest diff peak, hole (e Å^{-3})	0.288, −0.338	0.683, −0.371	0.534, −0.636	0.494, −0.334

1H, −CH=N−); 3.56 and 4.04 (m, 2H, =NCH$_2$−); 1.87 and 2.27 (m, 2H, −CH$_2$−); 2.26 and 2.74 (m, 2H, −CH$_2$N−); 2.49 (s, 3H, Me); 2.24 (s, 3H, Me); 3.75 (s, 6H, 2 OMe); 5.25 (s, 2H, CH$_2$Cl$_2$). $^{13}C\{^1H\}$ NMR:[44] δ 70.7 (C_5H_5); 81.2 (C^1); 76.6 (C^2); 72.3 (C^3); 72.1 (C^4); 76.4 (C^5); 168.4 (−CH=N−); 60.4 (=NCH$_2$−); 26.0 (−CH$_2$−); 59.7 (−CH$_2$N); 50.0 (Me); 48.5 (Me), 51.5 and 51.6 (2 OMe); 172.7 and 164.3 (2 −COO); 129.9 and 144.0 (C$^\alpha$ and C$^\beta$ of the alkene).

Crystal Structure Determination and Refinement. A prismatic crystal of **4a**,**b**, **5b**, or **8b** (sizes in Table 7) was selected and mounted on a MAR345 diffractometer with an image plate detector. Unit cell parameters were determined from automatic centering of 7351 (for **4a**), 7482 (for **4b**), 13 452 (for **5b**), or 13 816 (for **7b**) reflections in the range 3° ≤ θ ≤ 31° and refined by a least-squares method. Intensities were collected with graphite-monochromated Mo Kα radiation. The numbers of measured reflections were 19 243 (for **4a** in the range 1.90° ≤ θ ≤ 28.83°), 10 604 (for **4b** in the range 3° ≤ θ ≤ 31°), 13 452 (for **5b** in the range 3.02° ≤ θ ≤ 31.11°), and 8578 (for **8b** in the range 1.89° ≤ θ ≤ 31.65°). The numbers of reflections which were nonequivalent by symmetry were 4526 (R_{int}(on I) = 0.039) for **4a,** 4666 for **4b** (R_{int}(on I) = 0.036), 3606 (R_{int}(on I) = 0.034) for **5b,** and 8578 (R_{int}(on I) = 0.0475). The numbers of reflections assumed as observed, applying the condition $I > 2\sigma(I)$, were 2225 (for **4a**), 3537 (for **4b),** 3099 (for **5b**), and 6055 (for **8b)**. Lorentz−polarization corrections were made, but absorption corrections were not.

The structures were solved by direct methods using the SHELXS computer program[46] and refined by full-matrix least-squares methods with the SHELX97 computer program[47] using 4256 (for **4a**), 4666 (for **4b**), 3606 (for **5b**), and 8578 (for **8b**) reflections (very negative intensities were not assumed).

In the four cases the function minimized was $\sum w||F_o|^2 - |F_c|^2|^2$, with $w = [\sigma^2(I) + (0.0610P)^2]^{-1}$ (for **4a**), $w = [\sigma^2(I) + (0.0536P)^2]^{-1}$ (for **4b**), $w = [\sigma^2(I) + (0.0434P)^2]^{-1}$ (for **5b**), $w = [\sigma^2(I) + (0.0498P)^2]^{-1}$ (for **5b**), and $w = [\sigma^2(I) + (0.0610P)^2]^{-1}$ (for **8b**) and $P = (|F_o|^2 + 2|F_c|^2)/3$; ×c4, ×c4′, and ×c4″ were taken from the literature.[48] The chiralities of the structures of **4a** and **5b** were defined from the Flack coefficient,[49] which is equal to 0.04(3) for **4a** and 0.06(4) for **5b**.

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Supporting Information Available: Tables containing crystal data and structure refinement details, atomic coordinates and equivalent isotropic parameters, all bond lengths and angles, hydrogen bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates for compounds **4a**,**b**, **5b**, and **8b** (Tables S1−S21). This material is available free of charge via the Internet at http://pubs.acs.org.

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