Synthesis of η^3-allyl–Pd complexes and subsequent formation of N-heterocycles via the reaction of a cyclometallated compound with conjugated dienes

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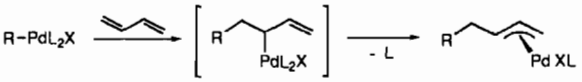
Abstract

The Pd–C bond of the cyclopalladated derivative of dimethylaminomethylferrocene (**1**) is fairly reactive to insertion of conjugated dienes such as 1,3-butadiene, isoprene, 2,3-dimethylbutadiene or 1,3-cyclohexadiene. This reaction affords organopalladium complexes containing an η^3-allyl–Pd moiety where the NMe_2 unit of the starting material is still intramolecularly coordinated to Pd. These complexes are stable in solution but in MeOH in the presence of PPh_3, reductive elimination of Pd is observed. This occurs whilst a nucleophilic intramolecular addition of the NMe_2 group to the allylic fragment takes place, affording six-, seven- or eight-membered heterocyclic compounds. The importance of the steric effects of the substituents on the butenyl chain upon the course of the reaction has been investigated.

Key words: Crystal structures; Palladium complexes; Allyl complexes; N-heterocycle complexes; Cyclometallation; Conjugated dienes; Insertion; Depalladation

Introduction

It is well known that conjugated dienes react with organopalladium compounds to afford, after insertion into the C–Pd bond, η^3-allyl–palladium complexes (see eqn. (1)) [1]. This functionalisation reaction has been used for numerous R–Pd moieties. However, it has never been described for cyclopalladated tertiary amines. This is rather surprising, since the Pd–C bond of cyclopalladated compounds are well-known to react with C–C multiple bonds. In the case of mono-substituted olefins, a so-called Heck reaction leads to substitution of one C–H unit of the alkene by the palladated substrate via an insertion–elimination process [2]. With internal alkynes the same starting materials afford usually (σ-η^2)-butadienyl–Pd complexes by insertion of two alkyne units into the C–Pd bond [3]. We have studied the synthetic potential of cyclopalladated compounds, especially in their reactions with alkynes, for the selective formation of carbo- and heterocyclic organic products [3, 4]. In order to enlarge the scope of the use of cyclopalladated compounds as organometallic 'synthons' in organic synthesis, we



(1)

R = halogen, aryl, alkyl, etc...

decided to study their reactions with other reagents, such as dienes.

In recent studies, the cyclopalladated complex of *N,N*-dimethylaminomethylferrocene (**1**) was shown to display a reactivity of its C–Pd bond very similar to that of known Ar–Pd complexes [4]. Moreover, the asymmetry due to the planar chirality of the ferrocenyl group appeared to be very useful in following the evolution of the structure of the organometallic species during the reaction [5]. This asymmetry also gives a

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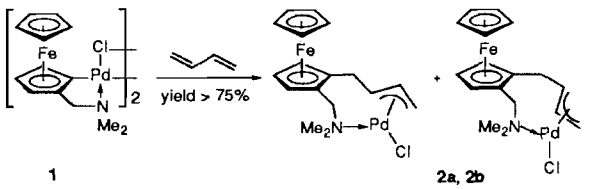
possible insight into the stereoselectivity of the bond formations occurring during the overall reaction. We report now on the reaction of complex **1** with conjugated dienes. In most cases stable organopalladium complexes were formed and isolated; their subsequent depalladation, to afford organic products, was induced by the addition of PPh_3. The effects of the diene substituents upon the insertion reaction, as well as the depalladation products, have been investigated.

Results

Reaction of the C–Pd bond with conjugated dienes

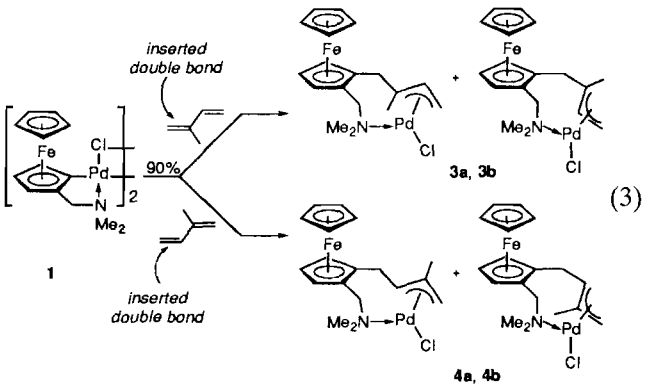
The reaction of **1** with an excess of 1,3-butadiene in CH_2Cl_2 at room temperature afforded, in good yield (75%), two inseparable complexes, **2a** and **2b**, in a 3 to 2 ratio. On the basis of their ^1H and ^{13}C NMR data, **2a** and **2b** were identified as two isomers of the η^3-allyl–Pd complex resulting from the insertion of the butadiene into the Pd–C bond of **1**. For both complexes, the $^3J_{HH}$ coupling constant values within the allylic fragment indicate that the *syn* complexes were formed. Moreover, spectroscopic evidence was found for amine–palladium coordination; for example, the methyl groups of the NMe_2 unit appear as two singlets. We therefore concluded that **2a** and **2b** have a monomeric structure in which the Pd(II) centre is ligated by a chlorine atom, the newly formed η^3-allyl unit and the nitrogen atom of the intramolecularly coordinating CH_2NMe_2 fragment.



(2)

The observation of the isomers **2a** and **2b** is the result of the existence of two blocked conformations of the non-planar palladacycle in relation to the asymmetric ferrocenyl moiety. The conversion of **2a** into **2b**, and vice versa, could involve a π–σ–π process as was often shown in related η^3-allyl complexes [1]. A related observation has been described recently for σ-η^2-butadienyl–Pd and η^3-allyl–Pd complexes containing the same ferrocenyl group [5]; however, in the present case no isomerisation from **2a** to **2b** or the reverse reaction could be induced thermally in contrast to what was observed in the previous case. Thus **2a** and **2b** are in fact conformers as shown in eqn. (2). This was unambiguously established by an NOE-NMR experiment on a related complex (see below), although, in the case of **2a** and **2b**, it was not possible to correlate the NMR data of one complex with a definite structure.

When complex **1** was reacted with 2-methyl-1,3-butadiene, a complete transformation took place and four products, **3a**, **3b**, **4a** and **4b**, were observed by NMR in a 1/1/4/2 ratio, respectively. For the minor isomers, **3a** and **3b**, the signal characteristic for the proton on the central carbon atom of a η^3-allyl–Pd moiety (5.0 and 4.65 ppm, respectively) was found by ^1H NMR whereas, for the major isomers, **4a** and **4b**, this proton signal was lacking. For the latter complexes, the methyl resonance of the butenyl chain substituent was shifted downfield with respect to **3a** and **3b**, characteristic for sp^2-C bound methyl groups (1.77 and 1.99 ppm, respectively). These spectroscopic data are consistent with the formation of the two insertion products of isoprene. Due to the disymmetry of this diene, the insertion of one or the other carbon–carbon double bond leads to the regioisomers **3** or **4** for which the position of the methyl substituent on the formed η^3-allyl–Pd moiety is different. The major regioisomer, **4**, results from the insertion of the less substituted C=C into the Pd–C bond of **1**. As in the case described previously with 1,3-butadiene, the regioisomers **3** and **4** exist both as two conformers. The proposed structures for the four isomers are given in eqn. (3).



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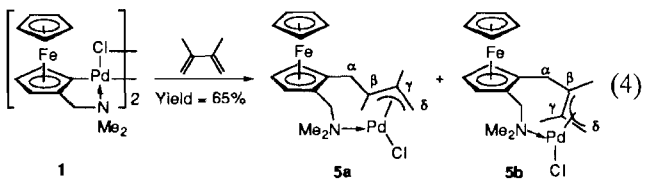
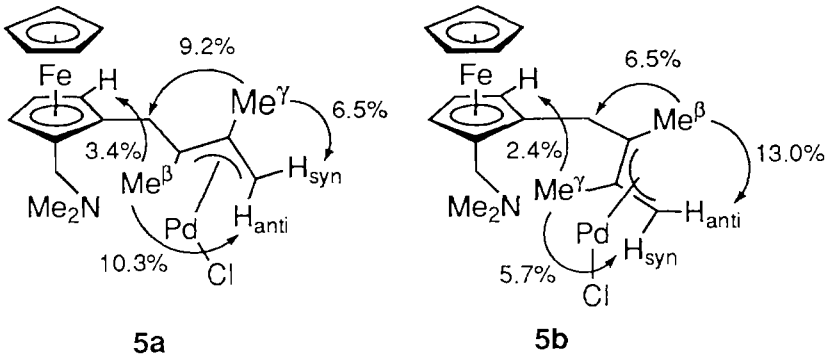


(4)

At room temperature, no reaction was observed between 2,3-dimethylbutadiene and complex **1**. In refluxing acetone, this reaction led to the two η^3-allyl–Pd conformers, **5a** and **5b**, in a 5 to 2 ratio. An NOE-^1H NMR experiment showed that for both **5a** and **5b** the methyl substituents on the allylic fragment have adopted an *anti* conformation as expected (see Scheme 1). Moreover, for **5a** the methyl group in position β (Me_β) appeared to be close to the *ortho* proton of the C_5H_3 moiety referring to the measured ^1H-NOE effect of 3.4%. For **5b**, the *ortho* proton was found close to the

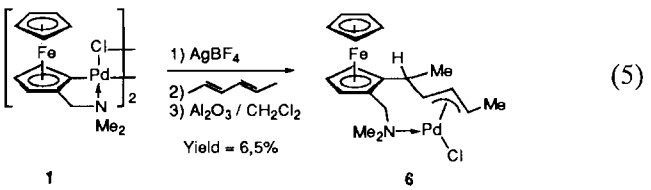


Scheme 1. Main ^{1}H-NOE effects observed for η^3-allyl–Pd complexes **5a** and **5b**.

methyl substituent in the γ position with an NOE effect of 2.4%. These facts are consistent with the structures proposed for the η^3-allyl–Pd conformers obtained before (*vide supra*). For **5a** and **5b**, we could now correlate the NMR data of each complex with a defined structure as presented in eqn. (4).

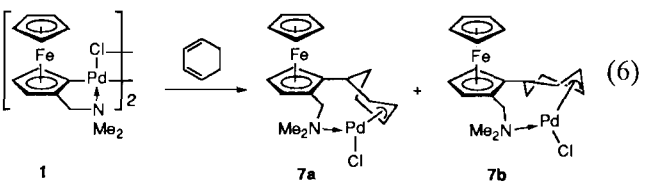
The internal diene, (*E*),(*E*)-2,4-hexadiene, appeared to be very inert towards the C–Pd bond. It reacted only with the cationic palladium complex obtained by treatment of **1** with $AgBF_4$. However the reaction was not selective and the expected η^3-allyl–Pd compound, **6**, could be isolated only in very poor yields (6.5%) from a mixture of several unidentified compounds (eqn. (5)). Complex **6** was obtained as the chlorinated complex due to work-up in the presence of a chlorinated solvent (see 'Experimental').

The ^{1}H NMR spectrum of **6** showed the presence of one conformer only, having a *syn*-arrangement around the η^3-allyl fragment ($^3J_{HH}$ = 7.5 and 12.3 Hz). The observation of one single isomer indicates that not only one palladacycle conformation is preferred but also that the stereogenic carbon centre, C_α, is formed stereoselectively with respect to the adjacent asymmetric ferrocenyl group.



(5)

To complete our study on diene insertion into the C–Pd bond of **1**, we investigated the reaction with 1,3-cyclohexadiene. As for the non-encumbered linear dienes, 1,3-cyclohexadiene reacted at room temperature to afford η^3-allyl–Pd complexes **7a** and **7b** in 70% yield. These complexes were not stable in solution and decomposition (i.e. formation of palladium black) occurred within a few hours. As for **6**, a new stereogenic carbon centre is formed during the insertion step; moreover, the possible boat and chair conformations of the cyclohexenyl ring introduce another isomer factor. The complexes could be structurally characterised by ^{1}H NMR spectroscopy which showed the existence of only two isomers, **7a** and **7b**, in a 13 to 1 ratio.



(6)

On the basis of steric considerations a likely structure for these complexes is that for which the ferrocenyl and the cyclohexenyl groups are staggered, **7a** and **7b** being the boat and chair isomers as drawn in eqn. (6). Recently, an X-ray study showed that in an η^3-(1,3-cyclohexenyl)Pd complex both chair and boat conformations of the cyclohexenyl ring may exist [6]. Based on molecular models the boat conformation for the cyclohexenyl ring seems to be the favoured one in our complexes and for this reason we propose the major isomer, **7a**, to have the cyclohexenyl group in such a conformation.

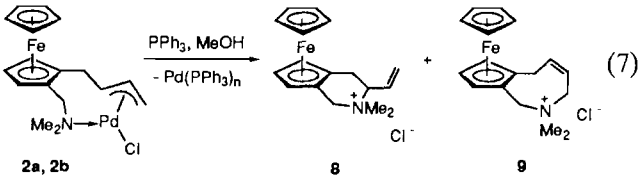
Depalladation reactions

The use of η^3-allyl–Pd intermediates for allylic functionalisation by reactions with several nucleophiles (amines, carbanions, alcohols, etc.) has found very broad applications in organic synthesis [7]. This metal-mediated coupling reaction proved to be also a powerful route for carbo-and heterocycle synthesis [8–10]. Numerous nitrogen heterocycles have been synthesised using this methodology. Nevertheless these procedures all involved primary or secondary amines as nucleophiles. We now report that with a tertiary amine as the nucleophile the cyclisation reaction also takes place

leading to cationic heterocycles. We reported observations when studying the palladium-mediated intramolecular C–N bond formation between tertiary amines and alkenes [11].

The η^3-allyl–Pd complexes described in the previous section are very stable most probably because of the intramolecular coordination of the NMe_2 group to Pd. However, recently we reported that (σ-η^2)-butadienyl-Pd complexes stabilised by intramolecular N-coordination are efficiently depalladated under mild conditions using PPh_3 to give carbo- and heterocycles [4a, b]. Applying this methodology to complexes **2**, **5** and **7** the resulting depalladated products could be obtained and analysed.

When **2a** and **2b** (as a mixture of the two conformers) and four equivalents of PPh_3 were reacted in MeOH at room temperature a quantitative depalladation reaction occurred affording $Pd(PPh_3)_n$ together with two ionic N-heterocyclic compounds, **8** and **9**, isolated in high yields in a 1 to 2 ratio (eqn. (7)). Their structures were deduced from analytical and spectroscopic data and found to be the six- and the eight-membered heterocycles, respectively. These products are the result of either *exo*- or *endo*-cyclisation by intramolecular C–N bond formation between the N atom and one of the termini C atoms (C_β or C_δ) of the η^3-allyl–Pd moiety of **2**.



(7)

We have observed that in the presence of Pd(0) these two heterocycles are in equilibrium. Indeed, when a mixture of **8** and **9** (1:2 ratio, respectively) was dissolved in acetone in the presence of $Pd(PPh_3)_4$ (1–2 mol%) the six-membered heterocycle **8** crystallised out of the solution and within a few hours a complete isomerisation of **9** into **8** had occurred. The driving force for this isomerisation is mainly due to a difference of solubilities of **8** and **9** which displaces the equilibrium. A solution of **8** and $Pd(PPh_3)_4$ (2 mol%) in MeOH gave back the mixture of the six- and eight-membered heterocycles in the same ratio (1 to 2) as that found initially from the depalladation of **2**. This isomerisation reaction most probably involves a nucleophilic displacement of the allylic ammonium group by Pd(0) [12] leading back to the organometallic η^3-allyl–Pd intermediate. We could

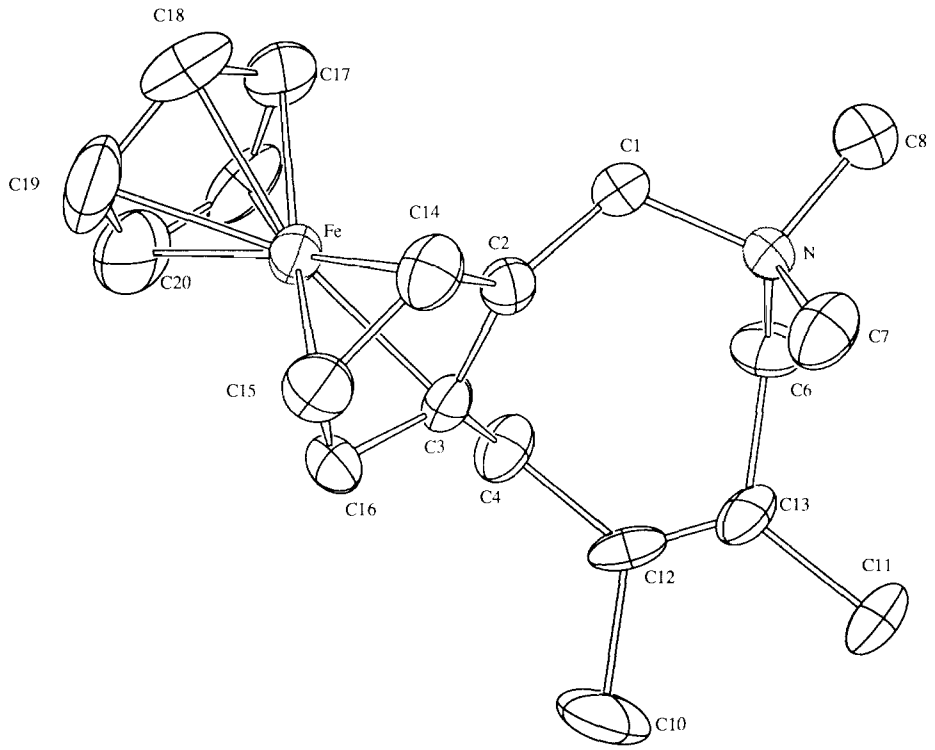
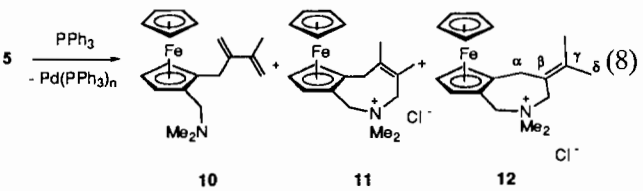


Fig. 1. ORTEP drawing of the cation of **11*** and adopted numbering scheme with thermal ellipsoids drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): N–Cl, 1.515(9); N–C(6), 1.55(1); C1–C2, 1.49(1); C2–C3, 1.44(1); C3–C4, 1.52(1); C4–C12, 1.58(3); C12–C13, 1.20(3); C11–C13, 1.59(4); C10–C12, 1.64(4); C6–C13, 1.66(4); C1–N–C6, 111.2(6); N–C1–C2, 115.6(6); C6–C13–C12, 114.0(4); C6–C13–C11, 121.0(2); C10–C12–C13, 115.0(4); C4–C12–C13, 124.0(5).

check by ^1H NMR spectroscopy that immediately after addition of PPh_3 to a solution of **2** the product ratio, **8**:**9**, was the same as that at the end of the depalladation reaction excluding the possibility that **8** or **9** can be the kinetic or the thermodynamic products of the reaction.

The depalladation of the methyl-substituted η^3-allyl–Pd complexes **5a** and **5b**, as described above for **2**, gave a mixture of three major products together with $Pd(PPh_3)_n$ (eqn. (8)). One product, **10** (36%), was isolated as a non-ionic orange oil and identified by ^1H and ^{13}C NMR spectroscopy to be the diene resulting from a β-hydrogen elimination process. The two other compounds, **11** and **12**, were formed in a 2 to 3 ratio and could not be separated from each other. The ^1H NMR spectral data of the mixture of **11** and **12** showed clearly the presence of four methyl-groups (as four singlets) for each compound, two of them being downfield shifted ($\delta = 3.3$–2.64 ppm) as previously observed for the quaternary NMe_2 group in **8** or **9**. The absence of olefinic proton signals allowed us to exclude the possibility of the two compounds being a mixture of the *endo*- and *exo*-cyclisation products as was the case for **8** and **9**.



10 11 12

The structures of **11** and **12** were unambiguously established in the solid state by an X-ray diffraction study. The specifics of this X-ray study will be discussed below. The ORTEP drawings of the cationic parts and the adopted numbering scheme are presented in Figs. 1 and 2 for **11*** and **12***, respectively (**11*** and **12*** are derived from **11** and **12** by substitution of the Cl^- anion for PF_6^-). The geometric data are given in Table 1.

The molecular structure of the cationic part of **11*** (Fig. 1) shows it to be an eight-membered nitrogen heterocycle resulting from bond formation (N–C6) between the NMe_2 group and the C_δ of the η^3-allyl–Pd part of **5** as described above for **9**. The *endo*-cyclic C=C double bond (C12–C13) is located on the methyl-substituted carbon atoms (initially C_β and C_γ in **5**) and displays *cis* geometry (see eqn. (4) for the significance of α to δ on the butenyl chain). In marked contrast,

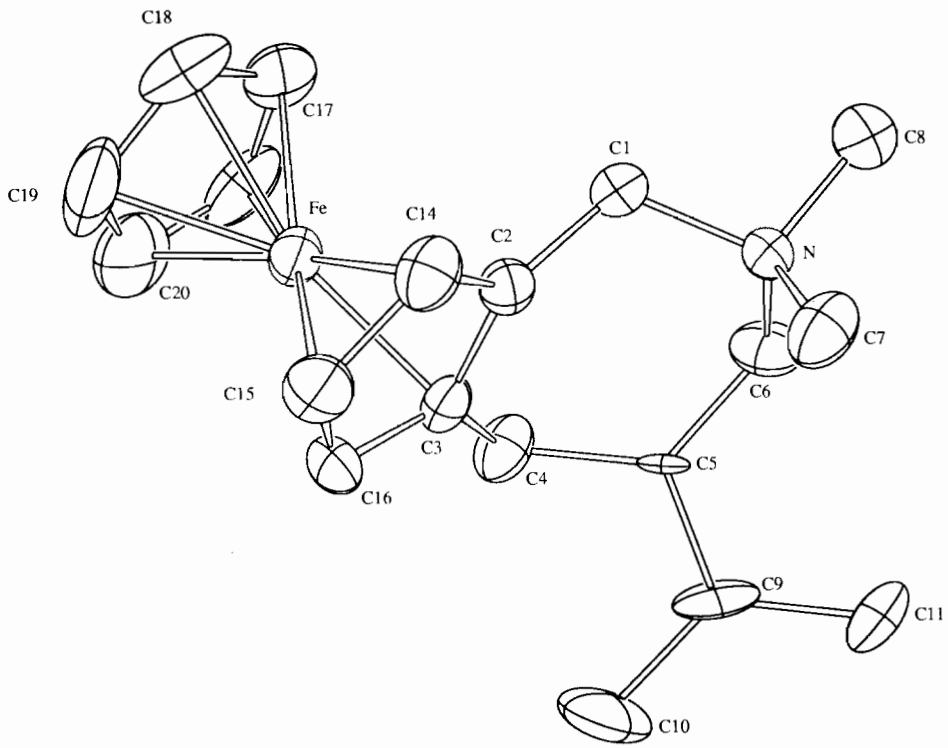


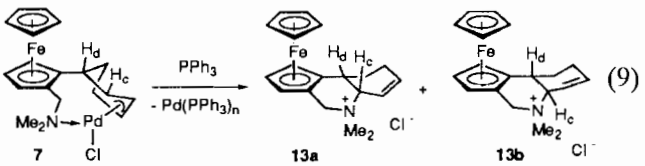
Fig. 2. ORTEP drawing of the cation of **12*** and adopted numbering scheme with thermal ellipsoids drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): C4–C5, 1.58(3); C5–C6, 1.54(3); C5–C9, 1.42(3); C9–C10, 1.57(4); C9–C11, 1.54(4); C4–C5–C9, 116.0(3); C6–C5–C9, 118.0(3); C5–C9–C10, 115.0(3); C5–C9–C11, 116.0(3); C10–C9–C11, 127.0(1).

TABLE 1. Crystal data and details of the structure determination of compounds **11*** and **12***

Formula	$C_{39}H_{52}N_2F_{12}P_2Fe_2$
Molecular weight	950.5
Colour	red
Crystal system	monoclinic
a (Å)	11.330(3)
b (Å)	16.890(5)
c (Å)	11.442(3)
β (°)	106.10(2)
Volume (Å^3)	2103.7
Z	2
D_{calc} (g cm^{-3})	1.500
Wavelength (Å)	0.7107
μ (cm^{-1})	8.456
Space group	$P2_1/n$
Diffractometer	Enraf-Nonius CAD4F
Crystal dimensions (mm)	$0.40\times0.20\times0.10$
Temperature (°C)	20
Radiation	Mo Kα graphite monochromated
Mode	$\theta/2\theta$
Scan speed	variable
Scan width (°)	$1.46+0.34\text{tg}\ (\theta)$
Octants	$\pm h+k+l$
θ min./max. (°)	2/24
No. data collected	4045
No. data with $I>3\sigma(I)$	1662
Absorption min./max.	0.99/1.00
$R(F)$	0.060
$R_w(F)$	0.083
p	0.08
GOF	1.575

the cationic part of compound **12*** (Fig. 2) was found to be a seven-membered N-heterocycle resulting from C–N bond formation (C6–N) between the nitrogen atom and the methyl substituent in the β position in **5**. This bond formation occurred concomitantly with a 1,4-H shift from the Me_β group (C6 in **12***) to the C_δ atom initially involved in the η^3-allyl–Pd interaction in **5** (C10 or C11 in **12***). The C=C double bond (C5–C9) is now found *exo*-cyclic and is still located between C_β and C_γ.

When the above described depalladation conditions were applied to complexes **7**, two compounds, **13a** and **13b**, were obtained in a 4 to 3 ratio. The major product, **13a**, could be isolated in a pure form by fractional crystallisation and its structure in solution was determined by ^{1}H NMR spectroscopy. Compound **13a** was found to be a fused five- and six-membered carbo- and heterocycle system resulting from C–N bond formation between the NMe_2 group and the η^3-cyclohexenyl–Pd moiety. From the coupling constant ($^3J_{HH}=6.1$ Hz) between H_c and H_d (see eqn. (9)) one can conclude that these two protons are *cis* to one another in **13a** and so the C–N bond must have occurred by *cis*-migration of the nitrogen atom onto the allyl–Pd moiety. Compound **13b** could not be isolated in a pure form but the ^{1}H NMR spectral data strongly suggest **13b** to have a structure very close to **13a**. We propose it to be the product from the same C–N bond formation process as for **13a**, compound **13b** thus being the isomer in which the H_c and H_d are *trans* to each other as a result of a *trans*-to-Pd substitution of the NMe_2 group onto the η^3-allyl–Pd moiety. This result is in line with related intramolecular bond formation reactions involving a η^3-allyl–Pd fragment being part of a carbocycle [9a–c].



The depalladation of the other complexes described here (i.e. **3**, **4** and **6**) was not investigated because the compounds were obtained in very low yields or as mixtures of isomers.

Solid state structure determination of 11 and 12**

Crystals suitable for an X-ray diffraction study were grown from a CH_2Cl_2 solution of **11*** and **12*** (in a 4 to 6 ratio) layered with Et_2O. The ^{1}H NMR spectrum of the crystals showed that both compounds were still present in more or less the same ratio. The X-ray diffraction analysis of what seemed however to be single crystals showed that **11*** and **12*** cocrystallise in the ratio 1:1 (see 'Experimental'). It is remarkable to note that with the exception of two carbon atoms for each compound (C12 and C13 for **11*** and C5 and C9 for **12***) all the other atoms of both cations are perfectly superimposed as illustrated in Fig. 3 which shows the pseudo-disorder involving these four atoms. This amazing result is thus due to the fact that the closely related compounds **11*** and **12*** have identical solubilities and cocrystallise in the same space group with unit cells having identical parameters within experimental errors. Final coordinates and equivalent isotropic thermal parameters are given in Table 2.

Discussion

The present results show that insertion of conjugated dienes into the C–Pd bond of a cyclopalladated tertiary amine leads selectively to stable η^3-allyl–Pd complexes under mild conditions, the latter complexes being easily depalladated to give cationic N-heterocycles. Only a very few examples of the formation of such heterocycles by nucleophilic addition of a tertiary amine to a polyenyl moiety have been previously reported [4a, b, 11, 13].

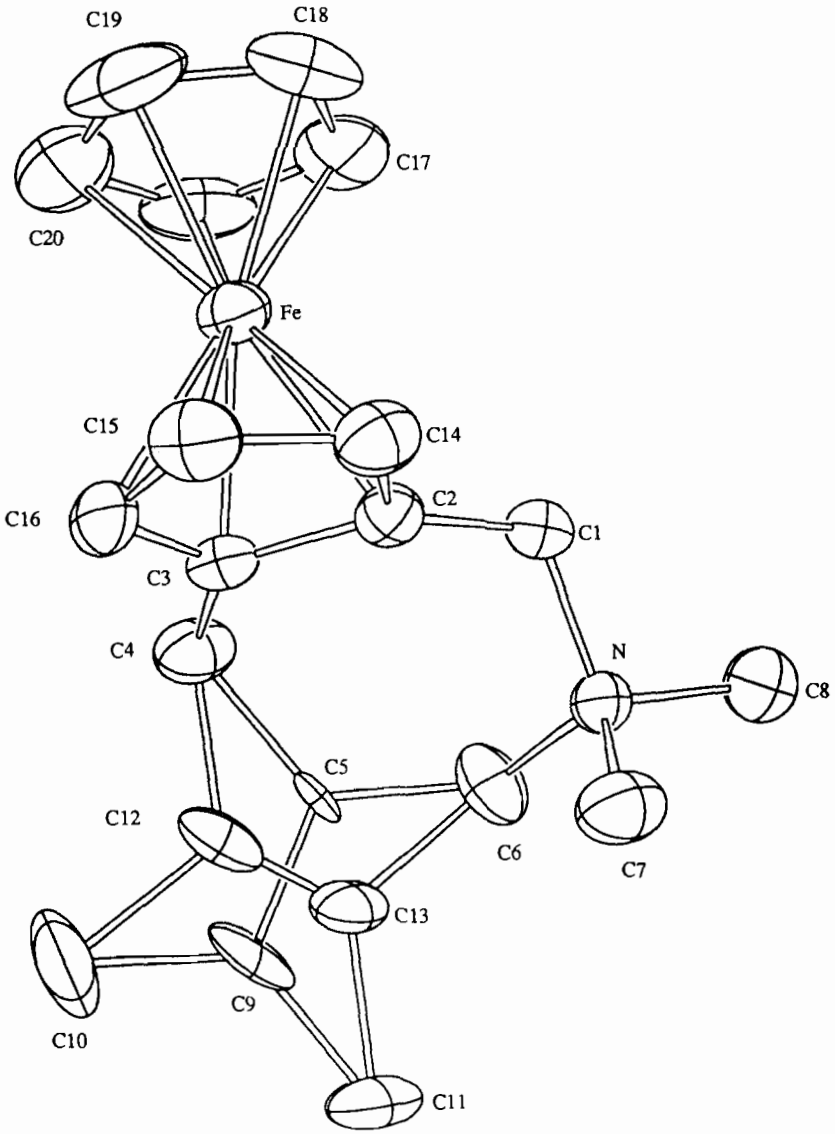


Fig. 3. ORTEP drawing of the superimposed cations of **11*** and **12*** showing the pseudo-disorder around the olefinic unit of the heterocyclic moiety.

In the reactions we have studied, the presence of a rather small substituent, an Me group, at different positions of the conjugated diene appears to have a direct effect on the insertion reaction, as well as on the nature of the products obtained after depalladation. For the insertion rate the substitution effect is clearly reflected by the conditions required for the reaction to take place and especially on the first step of the insertion reaction, i.e. the interaction between the olefin and the Pd centre. The major conclusion we can draw from these observations is that for terminal dienes a 2- or 2,3-substitution has only a rather limited influence on the insertion rate whereas in the case of a conjugated internal diene, i.e. the (*E*),(*E*)-2,4-hexadiene, the reaction requires drastic conditions to take place and moreover this leads to a non-selective reaction. The small steric perturbation due to a methyl substituent in position 2 is nicely illustrated by the reaction of 2-methyl-1,3-butadiene with **1**, for which the two insertion regioisomers, complexes **3** and **4**, are obtained (see eqn. (3)). The rather poor selectivity observed, a 1 to 3 ratio, respectively, reflects the small steric differences around both double bonds of the diene. The particular behaviour of 1,3-cyclohexadiene (it reacted with **1** like butadiene) may be explained by the all-*cis* geometric arrangement around the diene moiety that is likely to minimise the bulkiness of the molecule for interaction with the metal centre. The η^3-allyl–Pd complexes **2**, **5** and **7** were shown to be precursors of N-heterocycles since their depalladation induced by PPh_3 led almost exclusively to cyclisation products. In the cationic N-heterocycles obtained, the new C–N bond has been

TABLE 2. Final coordinates and equivalent isotropic thermal parameters of the non-hydrogen atoms of compounds **11*** and **12***

Atom	x	y	z	B (Å²)
Fe	0.0400(1)	0.21249(6)	0.3728(1)	3.59(2)
N	0.2311(5)	0.4118(3)	0.2509(5)	3.4(1)
C1	0.1809(7)	0.3285(4)	0.2498(7)	3.7(2)
C2	0.0819(6)	0.3185(4)	0.3115(7)	3.2(2)
C3	0.0989(7)	0.3210(4)	0.4409(7)	3.5(2)
C4	0.2192(7)	0.3455(5)	0.5300(7)	4.4(2)
C5	0.257(1)	0.4254(8)	0.478(1)	2.6(3)
C6	0.3215(8)	0.4320(5)	0.3765(7)	4.7(2)
C7	0.1272(8)	0.4699(5)	0.2135(8)	4.9(2)
C8	0.3038(8)	0.4133(5)	0.1631(8)	5.1(2)
C9	0.241(1)	0.4960(9)	0.539(1)	4.4(4)
C10	0.1677(9)	0.4862(7)	0.6367(8)	7.5(3)
C11	0.2734(9)	0.5739(5)	0.4853(9)	6.2(3)
C12	0.220(1)	0.4387(9)	0.536(1)	4.0(4)
C13	0.259(1)	0.4805(8)	0.470(1)	4.0(4)
C14	−0.0422(7)	0.2992(5)	0.2571(7)	4.3(2)
C15	−0.1028(7)	0.2904(5)	0.3487(7)	4.5(2)
C16	−0.0158(7)	0.3035(5)	0.4611(7)	4.5(2)
C17	0.1398(8)	0.1288(5)	0.3181(9)	6.2(2)
C18	0.0149(8)	0.1083(5)	0.2791(9)	6.1(3)
C19	−0.0261(9)	0.1027(5)	0.385(1)	8.2(3)
C20	0.071(1)	0.1174(6)	0.487(1)	8.1(3)
C21	0.1744(9)	0.1326(5)	0.4458(9)	6.7(3)
P	0.5371(2)	0.2042(1)	0.3652(2)	4.45(5)
F1	0.4177(6)	0.1825(5)	0.2651(6)	10.7(2)
F2	0.5235(7)	0.1298(4)	0.4414(6)	11.7(2)
F3	0.6582(5)	0.2284(4)	0.4658(5)	7.9(2)
F4	0.5438(7)	0.2808(4)	0.2934(6)	12.2(2)
F5	−0.5389(7)	0.2497(5)	0.4361(7)	14.9(3)
F6	−0.3896(7)	0.1651(6)	0.2923(7)	16.0(3)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

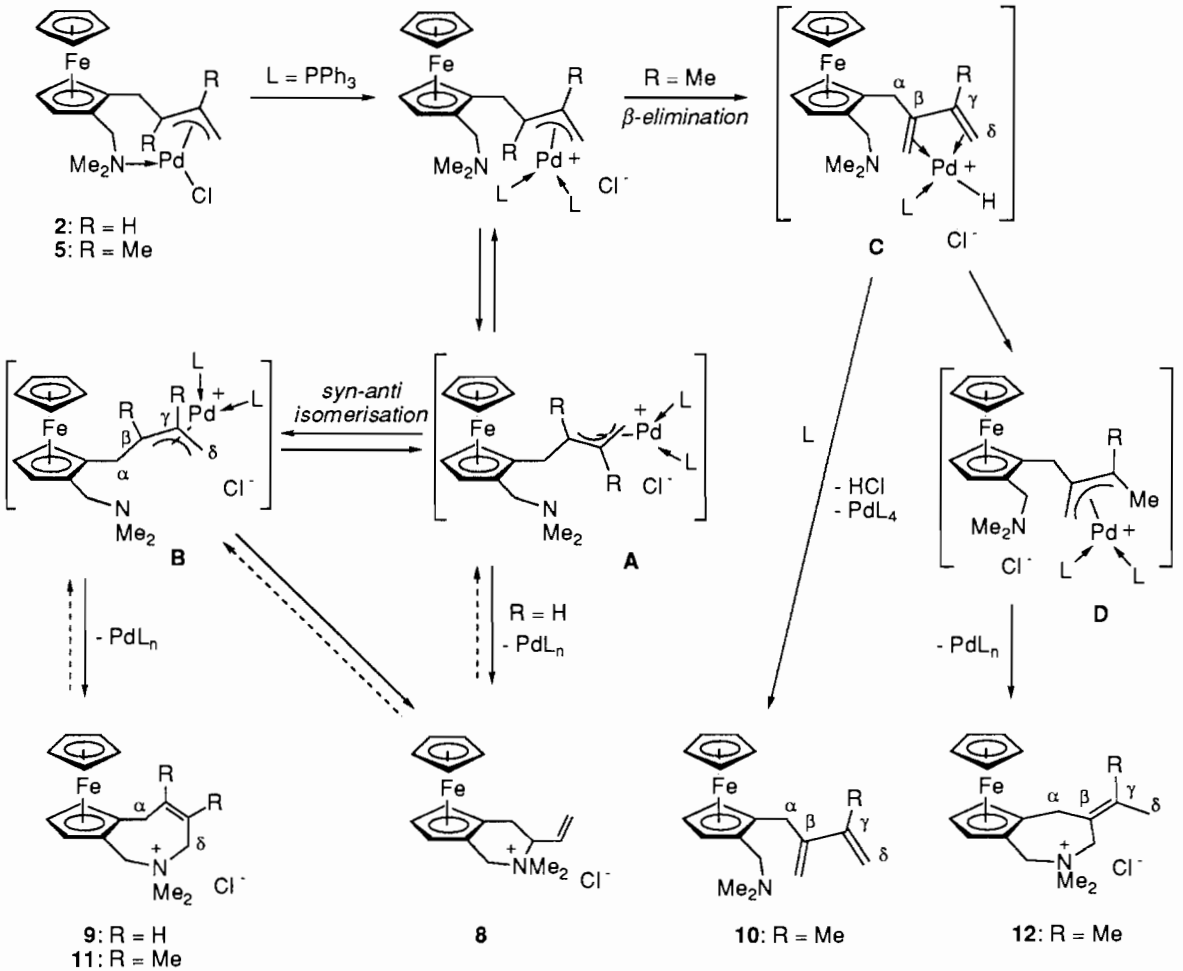
formed either at the more substituted carbon atom of the η^3-allyl–Pd moiety, C_β, affording compounds **8** or **12** via *exo*-cyclisation, or at the less substituted C_δ carbon atom, affording **9** and **11** via *endo*-cyclisation. The cyclisation pathway involves an intramolecular nucleophilic substitution of the non-coordinated NMe_2 group on the η^3-allyl unit. The role of the added PPh_3 in this reaction is not only to increase the electrophilicity of the η^3-allyl–Pd fragment, but mainly to displace by substitution the coordinated NMe_2 grouping from the palladium centre and so to generate the intramolecular nucleophile, i.e. the tertiary amine. This decoordination of the NMe_2 group allows the isomerisation of the η^3-allyl–Pd moiety to take place. When formation of the C–N bond leads to the generation of a new stereogenic C-centre as for **8**, only one diastereoisomer was observed. This points to the fact that only one isomeric form of the η^3-allyl–Pd complex is involved in the bond formation step of the reaction. The new stereogenic centre, formed stereoselectively, is imposed by the chirality of the ferrocenyl group. Starting with an optically pure complex **1**, heterocycle **8** should be obtained as a single enantiomer. The detailed depalladation pathways of **2** and **5** are presented in Scheme 2.

In the synthesised complexes, the thermodynamically more stable *syn* conformation of the η^3-allyl was found. However, in the eight-membered ring products **9** and **11**, the geometry of the *endo*-cyclic double bond was found to be *cis*. To rationalise this, it is necessary to assume that the intermediate η^3-allyl–Pd complex, **A** (see Scheme 2), undergoes a *syn–anti* isomerisation prior to C–N bond formation This *anti* isomer, **B**, allows nucleophilic substitution on the less substituted C_δ carbon atom of the allyl–Pd part to afford **9** and **11**. The *syn–anti* isomerisation is not required for the formation of the heterocycle **8**.

The formation of eight-membered heterocycles is rather unusual since for related organo–Pd precursors bearing an aryl instead of a ferrocenyl group, the cyclisation reaction involving a secondary [9c] or a tertiary amine [11] as nucleophile led sclectively to the six-membered rings with an *exo*-cyclic vinyl group. The origin of the formation of the eight-membered ring products may be related to the steric bulk of the ferrocenyl group close to C_β. Thus, the *exo*-cyclic C–N coupling is in competition with the alternative, sterically less hindered *endo*-cyclic coupling.

The effect of steric hindrance is dramatically demonstrated by the depalladation of the substituted complex **5** for which C_β (substituted by a methyl group) is no longer involved in a C–N bond formation. Moreover, the nucleophilic addition step was found to be in competition with another process leading to the major products, **10** and **12**, of the depalladation reaction. This competitive reaction involves the β-elimination of a H atom of the Me_β group affording the hypothetical palladium–hydride intermediate **C** (see Scheme 2). From this specics a reductive elimination of HCl leads to the new diene **10** [14]; whereas, the insertion of the double bond $C_\gamma{=}C_\delta$ in the Pd–H bond gives complex **D**. This latter reaction is thus an example of what may be considered as an overall 1,4-H shift. We are not aware of any related η^3-allyl–Pd moiety migrations via such an H shift. In a further step, nucleophilic attack of the NMe_2 group on the transient complex, **D**, thus formed, affords the seven-membered heterocycle **12**.

The cyclisation reaction affording compound **8** occurs with formation of a new stereogenic carbon centre. The fact that only onc diastcrcoisomer could be detected by ^1H NMR may indicate that the nucleophilic addition of a tertiary amine to a η^3-allyl–Pd unit follows a single pathway assumed to be the *trans*-to-palladium addition as expected for N-heterocycles [15]. As previously reported with η^3-cyclohexenyl–Pd complexes [9a–c], we



Scheme 2. Overall depalladation pathways for the η^3-allyl–Pd complexes.

observed deviation from that latter rule for the depalladation of complex **7**.

The present results show once again that under mild conditions and in very few steps, i.e. metallation–functionalisation–depalladation, a simple tertiary amine can be transformed selectively and with good yields into interesting organic heterocyclic compounds.

Experimental

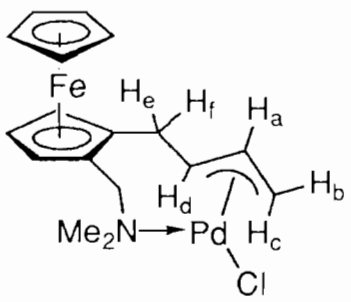
General considerations

All reactions were performed in Schlenk-type flasks under oxygen- and water-free nitrogen; solvents were dried and distilled under nitrogen prior to use. The ^{1}H NMR spectra were recorded at 200.13 or 300.13 MHz, ^{13}C NMR spectra at 50.32 or 75.47 MHz, on FT-Brucker instruments and externally referenced to TMS; J values are given in Hz and δ in ppm. Column chromatography was performed under N_2 by using Al_2O_3 as support (Al_2O_3 90, Activity II-III, 70–230 mesh, Merck). Elemental analyses were performed by the Service d'Analyses du CNRS at Strasbourg. Commercial compounds were used as received and complex **1** was synthesised according to a published method [16].

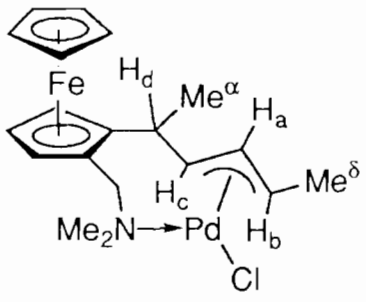
Diene insertion reactions

Complexes 2a and 2b

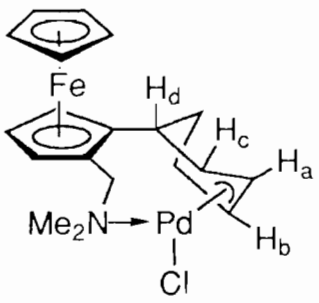
A solution of **1** (2.0 g, 2.6 mmol) and butadiene (2.2 g, 40 mmol) in CH_2Cl_2 (100 ml) was stirred at room temperature for 15 h. The resulting yellow solution was concentrated to 10 ml and chromatographed over Al_2O_3 (10×2.5 cm column, CH_2Cl_2). Elution with acetone afforded a yellow solution which was concentrated *in vacuo*. Hexane was added and the solution cooled to −30 °C. Complexes **2a** and **2b** (1.7 g, 75%) were isolated as yellow crystals. *Anal.* Calc. for $C_{17}H_{22}NFePdCl$: C, 46.7; H, 5.06; N, 3.19. Found: C, 46.7; H, 5.3; N, 3.0%. ^{1}H NMR ($CDCl_3$, 293 K): the numbering scheme of some protons is outlined in Chart 1. **2a**: δ=4.97 (m, 1H, H_a), 4.20–4.05 (m, 3H, C_5H_3), 4.06 (s, 5H, C_5H_5), 3.75 and 3.14 (2d, 2H, CH_2N,



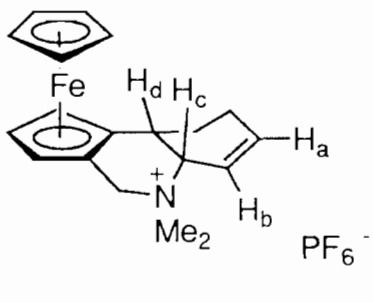
2



6



7



13a*

Chart 1. Numbering scheme of some protons used in 'Experimental'.

$^2J(HH) = 12.3$), 3.89 (broad d, 1H, H_c, $^3J(H_aH_c) = 10.9$), 3.53 (dd, 1H, H_b, $^2J(H_bH_c) = 1.3$; $^3J(H_aH_b) = 6.7$), 2.55 (broad d, 1H, H_d, $^3J(H_aH_d) = 11.6$), 2.88 and 2.50 (2s, 6H, NMe_2), 2.85–2.39 (m, 2H, $H_e + H_f$). **2b**: $\delta = 5.20$ (m, 1H, H_a), 4.20–4.05 (m, 3H, C_5H_3), 4.08 (s, 5H, C_5H_5), 4.06 (H_c under the C_5H_5 peak of **2a**), 3.86 and 3.04 (2d, 2H, CH_2N, $^2J(HH) = 12.6$), 3.62 (dd, 1H, H_b, $^2J(H_bH_c) = 1.4$; $^3J(H_aH_b) = 6.7$), 3.32 (m, 1H, H_d), 2.78 and 2.45 (2s, 6H, NMe_2), 2.85–2.39 (m, 2H, $H_e + H_f$). ^{13}C NMR ($CDCl_3$): **2a** and **2b**: $\delta = 109.8$ and 107.5 (CH_a), 85.9 and 84.9 (CH_d), 72.6; 71.0, 70.6, 69.6, 66.7 and 66.4 (C_5H_3), 69.2 (s, C_5H_5), 63.4 and 63.3 (CH_b), 54.4 and 54.1 (CH_2N), 52.1 and 46.3 (NMe_2, **2a**), 50.9 and 47.9 (NMe_2, **2b**), 30.4 and 27.8 (CH_e).

Complexes 3 and 4

A solution of **1** (384 mg, 0.5 mmol) and 2-methyl-1,3-butadiene (1.0 ml, 10 mmol) in CH_2Cl_2 (15 ml) was stirred at room temperature for 24 h. The resulting deep yellow solution was concentrated to 10 ml and chromatographed on alumina (10×2.5 cm column, CH_2Cl_2). Elution with CH_2Cl_2–acetone (1–1) afforded a yellow solution from which the mixture of isomers, **3a**, **3b**, **4a** and **4b** (406 mg, 90%) in a 1/1/4/2 ratio, was obtained as a yellow solid by removing the solvent *in vacuo*. *Anal.* Calc. for $C_{18}H_{24}NFePdCl$: C, 47.8; H, 5.3; N, 3.10. Found: C, 47.7; H, 5.5; N, 3.1%. ^1H NMR ($CDCl_3$, 293 K) characteristic signals of the mixture of isomers: **3a** and **3b**: $\delta = 5.0$ and 4.65 (2dd, 2H, CH), 3.98 and 3.96 (2s, 10H, C_5H_5), 1.14 and 0.70 (2s, 6H, Me); **4a**: $\delta = 3.95$ (s, 5H, C_5H_5), 2.82 and 2.37 (2s, 6H, NMe_2), 1.77 (s, 3H, Me); **4b**: $\delta = 3.99$ (s, 5H, C_5H_5), 2.67 and 2.35 (2s, 6H, NMe_2), 1.99 (s, 3H, Me). The other proton signals of the four isomers are superimposed between 4.20 and 2.20 ppm and could not be assigned.

Complexes 5a and 5b

A solution of **1** (767 mg, 1 mmol) and 2,3-dimethyl-1,3-butadiene (1.0 ml, 9 mmol) in acetone (15 ml) was refluxed for 20 h. The solvent of the resulting orange solution was evaporated *in vacuo*, the residue dissolved in CH_2Cl_2, filtered to remove traces of metallic palladium and chromatographed on alumina (10×2.5 cm column, CH_2Cl_2). Elution with acetone afforded a yellow solution from which **5a** and **5b** (0.61 g, 65%) were obtained in a 5 to 2 ratio after removing the solvent. *Anal.* Calc. for $C_{19}H_{26}NFePdCl$: C, 48.96; H, 5.62; N, 3.00. Found: C, 49.2; H, 5.2; N, 3.0%. ^1H NMR ($CDCl_3$, 293 K) **5a**: $\delta = 4.15$ and 4.08 (2m, 3H, C_5H_3), 4.06 (s, 5H, C_5H_5), 3.88 and 3.01 (2d, 2H, CH_2, $^2J(HH) = 12.6$), 3.45 (d, 1H, $=CH_{syn}$, $^2J(HH) = 1.8$), 2.96 (d, 1H, $=CH_{anti}$), 3.23

and 2.28 (2d, 2H, CH_2, $^2J(HH)=15.9$), 2.73 and 2.30 (2s, 6H, NMe_2), 2.09 and 0.76 (2s, 6H, Me). **5b**: $\delta=4.10$, 4.08 and 3.96 (3m, 3H, C_5H_3), 4.02 (s, 5H, C_5H_5), 3.79 and 3.21 (2d, 2H, CH_2N, $^2J(HH)=12.3$), 3.32 and 2.65 (2d, 2H, CH_2, $^2J(HH)=15.9$), 3.42 (s, 1H, $=CH_{anti}$), 3.03 (s, 1H, $=CH_{syn}$), 2.81 and 2.46 (2s, 6H, NMe_2), 1.86 and 1.24 (2s, 6H, Me). ^{13}C NMR ($CDCl_3$): **5a**: $\delta=117.2$, 89.9, 86.0, 78.5, 72.5, 71.3, 69.2, 66.5, 63.7, 54.6, 52.2, 46.0, 34.1, 21.3 and 20.5. **5b**: $\delta=121.0$, 89.4, 86.3, 80.9, 72.1, 70.9, 69.5, 65.7, 63.4, 56.7, 50.7, 47.2, 36.3, 25.7 and 20.6.

Complex 6

$AgBF_4$ (195 mg, 1 mmol) was added to a solution of **1** (384 mg, 0.5 mmol) in CH_2Cl_2 (20 ml) and MeCN (1 ml). After 5 min the AgCl precipitate was filtered off, the solvent removed *in vacuo* and the residue washed with Et_2O. The solid was dissolved in CH_2Cl_2 (15 ml), (*E*),(*E*)-2,4-hexadiene (0.11 ml, 1 mmol) was added and the solution stirred at room temperature for 15 h. The reaction mixture was concentrated and chromatographed on alumina (10×2.5 cm column, CH_2Cl_2). Elution with a CH_2Cl_2–acetone (1–1) mixture afforded a yellow solution from which complex **6** (30 mg, 6.5%) was obtained after solvent removal. *Anal.* Calc. for $C_{19}H_{26}NFePdCl$: C, 48.95; H, 5.6; N, 3.0. Found: C, 47.8; H, 5.4; N, 3.0%. ^1H NMR ($CDCl_3$, 293 K): the numbering scheme of some protons is outlined in Chart 1. $\delta=5.15$ (dd, 1H, H_a, $^3J(H_aH_b)=7.5$; $^3J(H_aH_c)=12.3$), 4.46 and 3.16 (2d, 2H, CH_2N, $^2J(HH)=12.3$), 4.23–3.99 (m, 10H, $C_5H_5+C_5H_3+H_c+H_b$), 2.70 and 2.46 (2s, 6H, NMe_2), 2.50 (m, 1H, H_d), 1.50 (d, 3H, Me_δ), 1.37 (d, 3H, Me_α).

Complexes 7a and 7b

A solution of **1** (384 mg, 0.5 mmol) and 1,3-cyclohexadiene (0.30 ml, 1.4 mmol) in $CHCl_3$ (10 ml) was stirred at room temperature for 10 h. The reaction mixture was subjected to flash chromatography over Al_2O_3 (10×2.5 cm column, CH_2Cl_2). Using acetone as eluent afforded a yellow fraction from which the solvent was removed *in vacuo* leaving a residue that was dissolved in CH_2Cl_2 (3 ml). From this solution complexes **7a** and **7b** (325 mg, 70%) were precipitated as a 13 to 1 mixture by addition of hexane. *Anal.* Calc. for $[C_{19}H_{24}NFePdCl+\frac{1}{4}C_6H_{14}]$: C, 50.70; H, 5.71; N, 2.88. Found: C, 50.7; H, 5.5; N, 2.9%. ^1H NMR ($CDCl_3$, 293 K): the numbering scheme of some protons is outlined in Chart 1. **7a**: $\delta=5.22$ (m, 1H, H_a), 5.09 (m, 1H, H_c), 4.97 and 3.04 (2d, 2H, CH_2N, $^2J(HH)=13.2$), 4.18 (s, 5H, C_5H_5), 4.12–3.96 (m, 4H, $C_5H_3+H_b$), 2.78 and 2.25 (2s, 6H, NMe_2), 2.20 (m, 2H, H_d+CH_2), 1.30 (m, 2H, CH_2), 0.87 (m, 1H, CH_2). **7b**: $\delta=5.51$ (m, 1H, H_a), 4.98 (m, 1H, H_b), 4.77 (dd, 1H, H_c, $^3J(H_cH_a)=6.8$; $^3J(H_cH_d)=2.9$), 4.57 and 3.19 (2d, 2H, CH_2N, $^2J(HH)=12.5$), 4.08 (s, 5H, C_5H_5), 2.61 and 2.40 (2s, 6H, NMe_2), 1.98, 1.92, 1.62 (3m, 3H, CH). ^{13}C NMR ($CDCl_3$, 253 K): **7a**: $\delta=102.0$, 94.0, 80.8, 79.5, 74.5, 72.1, 69.3, 66.1, 64.1, 54.1, 50.5, 36.6, 32.2 and 26.6.

Depalladation reactions

Formation of heterocycles 8 and 9

A suspension of **2** (438 mg, 1 mmol) and PPh_3 (1.05 g, 4 mmol) in MeOH (20 ml) was stirred at room temperature for 1 h. The yellow precipitate was filtered off, washed with MeOH (5 ml) and the solvent of the filtrate removed *in vacuo*. The residue was extracted with MeOH (5 ml), filtered and the solvent removed *in vacuo*. This step was repeated twice. The residue was then dissolved in CH_2Cl_2 (3 ml) and addition of Et_2O to the solution afforded **8** and **9** (300 mg, 90%) in a 1 to 2 ratio as a yellow precipitate. *Anal.* Calc. for $C_{17}H_{22}NFeCl$: C, 61.56; H, 6.68; N, 4.22. Found: C, 61.1; H, 6.7; N, 4.1%. ^1H NMR (CD_2Cl_2, 293 K): **8**: $\delta=6.12$ (dd, 1H, $=CH_2$, $^3J(HH)=17.7$), 5.90 (m, 1H, =CH), 5.78 (dd, 1H, $=CH_2$, $^3J(HH)=9.71$; $^2J(HH)=1.8$), 5.15 (m, 1H, CH), 5.35 and 4.58 (2d, 2H, CH_2N, $^3J(HH)=14.6$), 4.34 (s, 5H, C_5H_5), 4.23–4.15 (m, 3H, C_5H_3), 3.60 and 2.83 (2s, 6H, NMe_2), 3.07 (broad d, 1H, CH_2), 2.70 (dd, 1H, CH_2, $^2J(HH)=17.2$; $^3J(HH)=11.5$). **9**. $\delta=6.48$ (m, 1H, =CH), 5.69 (m, 1H, =CH), 4.64 and 4.05 (2d, 2H, CH_2N, $^2J(HH)=12.5$), 4.37; 4.32 and 4.27 (3m, 3H, C_5H_3), 4.20 (s, 5H, C_5H_5), 3.79 and 3.45 (2m, 4H, CH_2), 3.12 and 2.93 (2s, 6H, NMe_2). ^1H NMR (D_2O): **8**: $\delta=5.92$ (m, 1H, =CH), 5.73 (d, 1H, $=CH_2$, $^3J(HH)=16.8$), 5.65 (d, 1H, $=CH_2$, $^3J(HH)=10.2$), 4.70 and 4.18 (2d, 2H, CH_2N, $^2J(HH)=14.8$), 4.37 (m, 1H, =CH), 4.26 and 4.24 (2s, 2H, C_5H_3), 4.18 (s, 6H, $C_5H_5+C_5H_3$), 3.06 and 2.68 (2s, 6H, NMe_2), 3.01 and 2.71 (2m, 2H, CH_2). **9**: $\delta=6.25$ (m, 1H, =CH, $^3J(HH)=6.5$ and 10.9), 5.48 (m, 1H, =CH), 4.51 and 3.76 (2d, 2H, NCH_2, $^2J(HH)=13.4$), 4.16 and 4.07 (2m, 3H, C_5H_3), 3.99 (s, 5H, C_5H_5), 3.47 and 3.13 (2m, 4H, CH_2), 2.81 and 2.62 (2s, 6H, NMe_2). ^{13}C NMR (D_2O): **8**: $\delta=130.0$ and 128.3 (=CH), 81.0; 75.6; 68.9; 66.8 and 65.9 (C_5H_3), 73.7 (CH), 71.8 (C_5H_5), 66.3 (t, CH_2N, $^1J(CN)=2.8$), 54.1 and 43.7 (2t, NMe_2, $^1J(CN)=4.0$ and 3.5), 28.4 (CH_2). **9**: $\delta=142.7$ and 118.7 (=CH), 88.6; 73.4; 72.9; 71.6 and 69.5 (C_5H_3), 71.3 (C_5H_5), 62.4; 58.6 and 29.6 (CH_2); 51.4 and 51.0 (NMe) (the ^{13}C signals corresponding to the eight-membered ring appeared broad and with weak intensity).

Compounds 10, 11 and 12

A suspension of **5** (0.68 g, 1.45 mmol) and PPh_3 (1.52 g, 5.8 mmol) in MeOH (15 ml) was stirred at room temperature for 1 h. The yellow precipitate was filtered off, washed with MeOH (5 ml) and the solvent of the filtrate removed *in vacuo*. The residue was extracted with MeOH (5 ml), filtered and the solvent

removed *in vacuo*. The residue was dissolved in MeOH (10 ml) and Na_2CO_3 (0.5 g) was added. After *c.* 5 min the solvent was removed and the remaining solid extracted first with Et_2O (3×10 ml) then with CH_2Cl_2 (2×15 ml). The Et_2O extract was concentrated and chromatographed over Al_2O_3 [15×1 cm column, pentane–Et_2O (9/1)]. The pentane–Et_2O (9/1) mixture was used as the eluent until the excess PPh_3 was removed. Elution with Et_2O afforded then an orange fraction from which **10** (0.17 g, 36%) was obtained as an oil by removing the solvent *in vacuo*. The CH_2Cl_2 extract was reduced to *c.* 3 ml and addition of Et_2O and hexane caused the precipitation of **11** and **12** (0.18 g, 34%) in a 2 to 3 ratio. The anion exchange, Cl^- for PF_6^-, was performed by adding NH_4PF_6 to a solution of **11** and **12** in MeOH affording **11*** and **12***. *Anal.* Calc. for $C_{19}H_{26}NF_6FeP$ (**11*** + **12***): C, 48.63; H, 5.58; N, 2.98. Found: C, 48.88; H, 5.57; N, 3.01%. ^1H NMR: **10** ($CDCl_3$): $\delta = 5.16$ and 4.99 (2s, $=CH_2$), 5.14 and 4.87 (2s, $=CH_2$), 4.22 and 4.07 (2m, 2H, C_5H_3), 4.03 (s, 6H, $C_5H_5 + C_5H_3$), 3.40 (s, 2H, CH_2), 3.35 and 3.25 (A-B pattern, 2H, CH_2N, $^2J(HH) = 13.0$), 2.14 (s, 6H, NMe_2), 1.94 (s, 3H, Me). **11** (CD_3OD): $\delta = 4.74$ and 3.92 (2d, 2H, CH_2, $^2J(HH) = 13.4$), 4.22 (s, 5H, C_5H_5), 3.87 and 3.68 (2d, 2H, CH_2, $^2J(HH) = 13.1$), 3.29 and 2.64 (2s, 6H, NMe_2), 2.10 and 1.98 (2s, 6H, Me). **12** (CD_3OD) $\delta = 5.10$ (d, 1H, CH_2, $^2J(HH) = 13.4$), 4.21 (s, 5H, C_5H_5), 3.79 and 2.72 (2d, 2H, CH_2, $^2J(HH) = 13.4$), 3.59 and 3.28 (2d, 2H, $^2J(HH) = 17.9$), 3.19 and 2.86 (2s, 6H, NMe_2), 1.76 and 1.71 (2s, 6H, Me). The other proton signals of **11** and **12** are superimposed between 4.4 and 4.0 ppm and could not be assigned. ^{13}C NMR ($CDCl_3$): **10**: $\delta = 146.5$ and 142.8 (=C), 113.7 and 112.7 ($=CH_2$), 86.3; 83.1; 69.5; 69.4 and 66.0 (C_5H_3), 69.3 (C_5H_5), 57.5 and 31.7 (CH_2), 45.2 (NMe_2), 21.2 (Me).

Heterocycles 13a and 13b

Complex **7** (240 mg, 0.52 mmol) and PPh_3 (550 mg, 2.05 mmol) were reacted as described for **8** and **9** affording **13a** and **13b** (140 mg, 39%) in a 4 to 3 ratio as a yellow solid. Because of better NMR resolution the Cl^- anion was exchanged for PF_6^- affording **13a*** and **13b***. Compound **13a*** could be isolated in a pure form by recrystallisation from a CH_2Cl_2 solution layered with Et_2O. *Anal.* Calc. for $C_{19}H_{24}NF_6FeP$ (**13a***): C, 48.84; H, 5.18; N, 3.00. Found: C, 48.9; H, 5.1; N, 2.9%. ^1H NMR: the numbering scheme of some protons is outlined in Chart 1. ^1H NMR: **13a*** (CD_2Cl_2): $\delta = 6.55$ (m, 1H, H_a), 5.98 (m, 1H, H_b), 4.97 and 4.55 (2d, 2H, CH_2N, $^2J(HH) = 14.7$), 4.33–4.21 (m, 3H, C_5H_3), 4.26 (s, 5H, C_5H_5), 4.13 (m, 1H, H_c, $^3J(H_cH_d) = 6.1$), 3.83 and 3.51 (2s, 6H, NMe_2), 2.80–2.01 (m, 5H, $CH_2 + H_d$). **13b*** (main peaks, $(CD_3)_2CO$): $\delta = 5.06$ (d, 1H, CH_2N, $^2J(HH) = 15.2$), 4.38 (s, 5H, C_5H_5), 3.54 and 2.94 (2s, 6H, NMe_2).

X-ray structure determination of 11 and 12**

Suitable single crystals of **11*** and **12*** were obtained as described. One single crystal was cut out from a cluster of crystals and mounted on a rotation-free goniometer head. A systematic search in reciprocal space using a Enraf-Nonius CAD4-F automatic diffractometer showed this crystal belongs to the triclinic system.

Quantitative data were obtained at room temperature. All experimental parameters used are given in Table 1. The resulting data set was transferred to a VAX computer, and for all subsequent calculations the Enraf-Nonius SDP/VAX package [17] was used.

Three standard reflections measured every hour during the entire data collection period showed no significant trend. The raw data were converted to intensities and corrected for Lorentz, polarisation and absorption factors, the latter coming from the psi scans of four reflections.

The structure was solved using the heavy atom method. Inspection of the Fourier maps revealed that **11*** and **12*** are both present in the unit cell with all atoms superimposed except C12 and C13 for **11*** and C5 and C9 for **12***. The structure was therefore refined as disordered with an occupancy ratio of 1 to 1 resulting from the relative peak heights of the difference map calculated without the non-common atoms. Occupancy refinements of C12, C13, C5 and C9 confirmed the 1:1 ratio. After refinement of the heavy atoms, a difference–Fourier map revealed maximas of residual electronic density close to the positions expected for hydrogen atoms with the exception of those of the disordered part; they were introduced in structure factor calculations by their computed coordinates (C–H = 0.95 Å) and isotropic temperature factors such as $B(H) = 1.3\, B_{eq}$ (C) Å^2 but not refined. Full least-squares refinements: $\sigma^2(F^2) = \sigma^2$ counts $+ (pI)^2$. A final difference map revealed no significant maxima. The scattering factor coefficients and anomalous dispersion coefficients were taken from ref. 18.

Supplementary material

Tables of bond distances and angles, H atom coordinates, and thermal parameters (16 pages) are available from the authors on request.

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