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Further insight into the Mechanism of the Palladium Induced Carbocyclisation of Aryl Rings.

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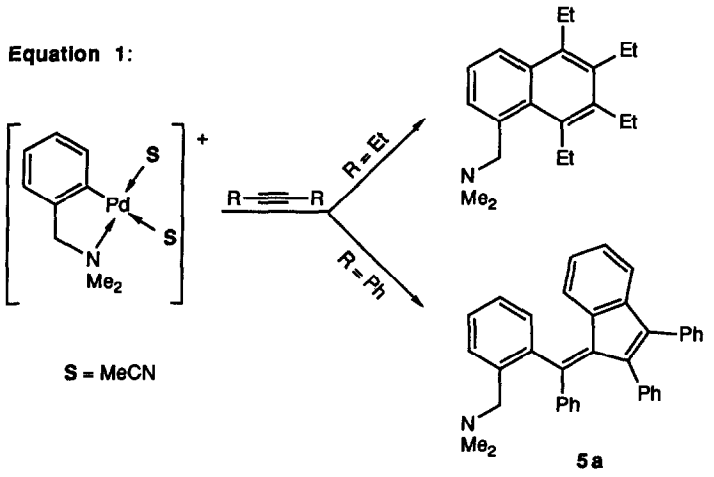
Abstract: *The depalladation of several cyclopalladated compounds, containing two inserted diphenylacetylenes in the Pd-C bond has been acheived by treament with either a neutral coordinating ligand such as pyridine, triphenylphosphine or maleic anhydride. This has afforded carbocyclic compounds where one or two of the aryl groups of the butadienyl chain have been annulated as a result of C-C bond formation. These demetallation reactions could be performed under rather mild conditions which enabled the characterisation of an intermediate which in turn provided valuable information about the mechanism of the palladium mediated carbocyclisation reaction.*

INTRODUCTION

Several examples of annulation reactions have been reported in the literature. In several cases these reactions involve the carbocyclisation of aryl groups, where ring formation result from the cleavage of an aromatic C-H bond. It has been extensively demonstrated by *Dötz* et al.[1] and others,[2] that a three component reaction can occur to afford such carbocyclisations by the reaction of aryl chromium carbene complexes with alkynes and CO. *Hidai* et al.[3] and *Buchwald* et al.[4] have observed the annulation of aryl rings with alkenes and CO which are mediated by palladium and zirconium complexes respectively. It has also been shown that the palladium mediated coupling reaction between alkenes and aryl halides (usually referred to as the Heck reaction) leads to carbocyclisation of the aryl group when β-elimination can not occur. For instance, *Chuisoli* et al.[5] and *De Meijere* et al.[6] have found that with norbornene the carboannulation of the aryl unit takes place. Similar results have also been found with the reaction of alkynes and aryl halides in the presence of palladium.[7] Recently *Heck* et al.[8,11] have found that

orthopalladated N,N dimethylaminomethyl benzene afforded either a naphthyl or a fulvene derivative by reaction with hex-3-yne or diphenyl acetylene,respectively (Equation 1).

Equation 1:

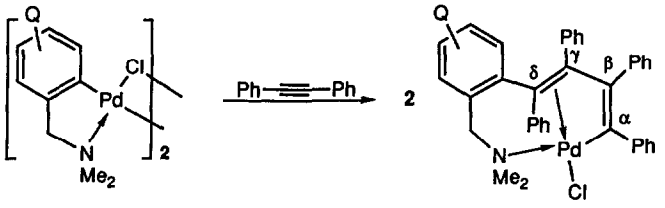


S = MeCN

5a

In the case of chromium mediated reactions a ketene intermediate is often proposed, preceeding the final C-C bond formation at the aryl ring.[1] However, the reaction pathway for palladium mediated processes has still to be firmly established, particularly for those reactions which take place in the absence of CO. We have found, in connection with the work of *Heck* et al., that carboannulation reactions of aryl groups can indeed be observed when the depalladation of compounds of type **3** is induced. The latter are formed through the insertion of two equivalents of diphenylacetylene in the palladium-carbon bond of **1** (Equation 2). We have discovered several ways to demetallate compounds **3** so that the annulation reaction can occur under rather mild conditions. It was thus possible to characterise a key-intermediate in one such carbocyclisation reaction which has allowed us to propose a more detailed mechanism. Some of these results have been published in a preliminary form.[9]

Equation 2:



1a Q = H
1b Q = 4,5 - CH_2O_2
1c Q = 4 - Me

3a Q = H
3b Q = 4,5 - CH_2O_2
3c Q = 4 - Me

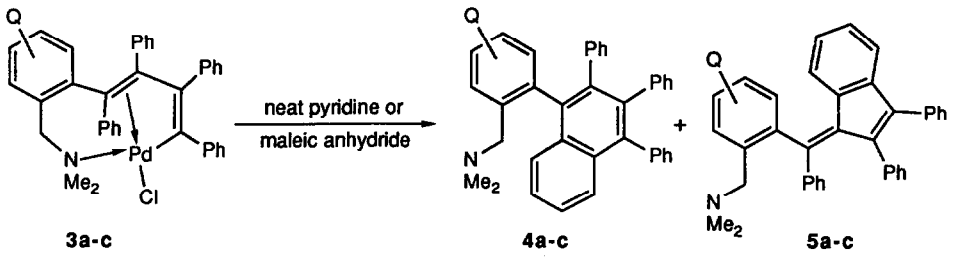
RESULTS AND DISCUSSION

Insertion of two diphenylacetylenes in the Pd-C bond of the cyclometallated N,N-dimethylaminomethyl benzene derivatives, **1**, or N,N-dimethylaminomethylferrocene, **2**, is straightforward and affords good yields of the neutral compounds **3** and **6** in which a polysubstituted butadienyl unit is η^3-bonded to Pd.[10,11]

We have found that it is possible to induce the depalladation of **3** and **6** by treatment with neutral ligands. Thus, when a solution of **3a** in neat pyridine was kept at reflux temperature for several hours it afforded, after work-up, an organic product **4a**. The ^{1}H NMR spectrum of **4a** (pale yellow compound) is significantly different from that of **5a** (orange red)[11] which is formed under different condition.

Treating compound **3b** in a similar fashion (*i.e.* reflux in pyridine) afforded two palladium free products, **4b** and **5b** in a ratio 4:1. The major isomer, **4b**, whose structure was confirmed by X-ray analysis,[9b] could be obtained pure *via* fractional crystallisation. Its ^{1}H NMR spectrum showed close analogies to that of **4a**, but with the presence of two doublets centered at 5.98 ppm due to the dioxymethylene protons. Furthermore the spectrum of **4b** shows a broad singlet at 2.05 ppm for both methyl groups and an AB spin system for the benzyl methylene group. Significantly, both protons on the carbon atom adjacent to the dioxymethylene bridge are still present. This indicates that no annulation of the starting benzyl ligand as described in equation **1** occurs. Protonation of the nitrogen atom of **4b** with HBF_4 in Et_2O results in the appearence of the methyl groups as two sharp doublets. Adding deuterated pyridine to this sample causes the methyl resonances to collapse to a broad singlet. During these experiments the methylene protons remain diastereotopic because of hindered rotation about the naphthyl-phenyl bond in **4**. The second product from the reaction of **3b** with pyridine, **5b**, was not isolated in a pure form. However, it is very likely that it has a fulvene type structure by analogy with **5a**.

Equation 3:



3a-c **4a-c** **5a-c**

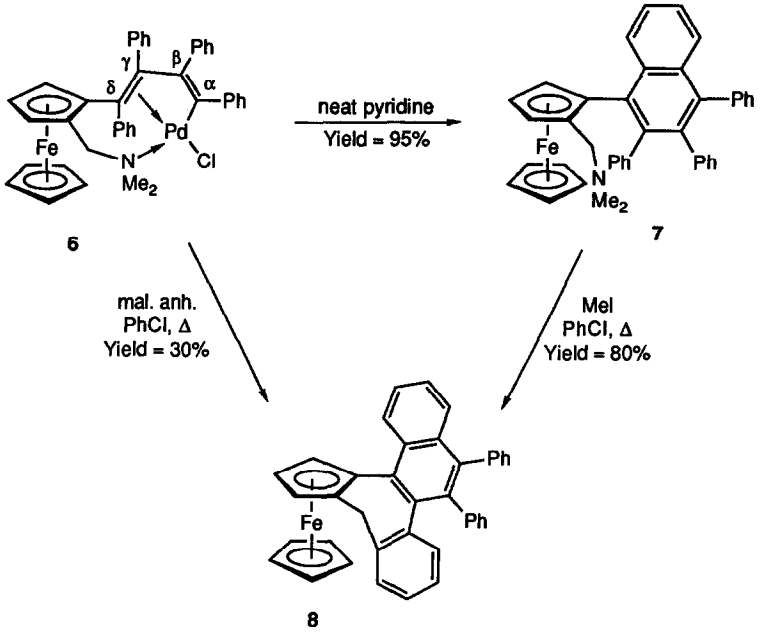
Schwartz et al. have found that electrophilic alkenes such as maleic anhydride and benzoquinone (π acid ligands) often promote C-C coupling in diorgano Pd(II) species.[12] Thus, when a chlorobenzene solution of **3b** was heated under reflux in the presence of excess maleic anhydride, rapid depalladation occurred to give a pale yellow solution after removal of the Pd metal. After work-up (*i.e.* treatment with NaOAc, see experimental section), the major organic product obtained appeared again to be **4b**, whilst only traces of **5b** could be observed in the ^{1}H NMR spectrum of the crude reaction product. Unexpectedly, no reaction occurred when **3a** was refluxed in chlorobenzene in the presence of maleic anhydride. By changing the solvent to bromobenzene (b.p. 160°C) traces of **4a** as well as some non-selective decomposition products were obtained.

Reaction of **3c** with maleic anhydride gave, after work-up, a mixture of products in a 3:1 ratio **4c**, **5c**. The high field shifted doublet at 6.20 ppm in the ^{1}H NMR spectrum of the minor isomer is characteristic of an aromatic proton of a fulvene derivative. Therefore the compounds formed should be **4c** and **5c** respectively.

In connection with the results reported here it is worth mentionning that related annulation reactions have been reported recently with a ligand similar to N,N-dimethylaminomethyl benzene; N,N-dimethyl-1,2,3,4-tetrahydronaphthyl-1-amine. We have found that similar annulation reactions take place when treating this compound with maleic anhydride.[13]

When compound **6** was treated with maleic anhydride compound **8** was formed in *ca.* 30% yield. The structure of the latter was elucidated by a crystal structure analysis.[9a] This showed that a double annulation reaction had occured on the γ and δ phenyl groups of the butadienyl chain, the second annulation resulting in loss of the NMe_2 group.

Equation 4:



6 **7** **8**

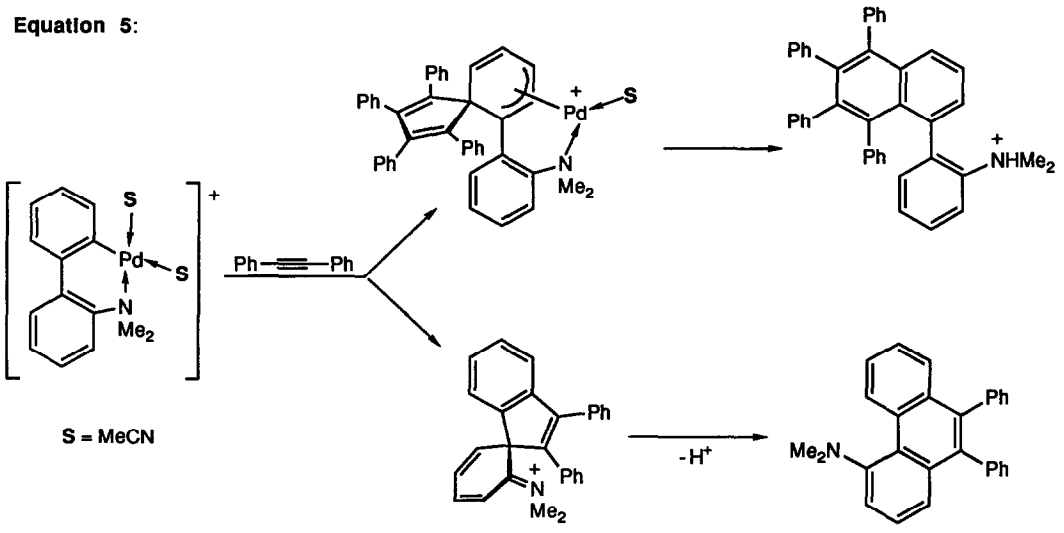
The thermal degradation of compound **6** in refluxing pyridine or in the presence of triphenylphosphine in methanol at room temperature gave high yields of the monoannulated compound **7**, which was shown to be indeed the precursor of **8**. When **7** was pyrolysed in the presence of maleic anhydride, **8** was formed in low yields as for the direct route from **6**. Quaternarisation of the NMe_2 group of **7** with MeI afforded the desired ammonium salt which led quantitatively to **8** by treatment in refluxing chlorobenzene for 0.5 h. This result shows that the synthesis of **8** occurs *via* a carbocation, easily produced from the ammonium intermediate,[14] which then undergoes an electrophilic substitution on the γ aryl ring of the butadienyl chain.

MECHANISM FOR THE ANNULATION OF ARYL RINGS.

We have previously shown that a cyclopalladated compound related to those used in this study led to the annulation of aryl rings through reaction with one or two equivalents of diphenylacetylene (Equation 5). In each

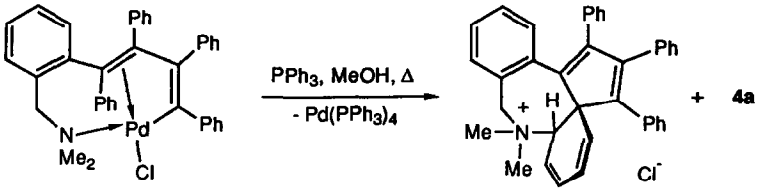
case spirocyclic compounds could be characterized.[15] These were shown to be genuine intermediates of either phenanthrene or polysubstituted naphthalene compounds. Earlier, related results were found for the carbocyclisation reactions of aryl induced by alkali metals.[16] There is thus good evidence that in our case the annulation reactions also occur *via* spirocyclic compounds.

Equation 5:



The depalladation of compound **3a** in the presence of four equivalents of PPh_3 in methanol at reflux temperature produced a mixture of **4a** and **9** in *ca.* 60% and 25% yield, respectively. The analysis and spectroscopic data allowed us to propose the geometry depicted in Equation 6 for the new compound **9**. Particularly diagnostic of this structure are the diastereotopic CH_2NMe_2 unit, the presence of four protons of a 1,3-diene moiety, and the existence of a tertiary carbon atom whose hydrogen atom resonates at 4.35 ppm . Furthermore ^1H NOE NMR experiments confirm the proposed structure (see Figure 1).

Equation 6:

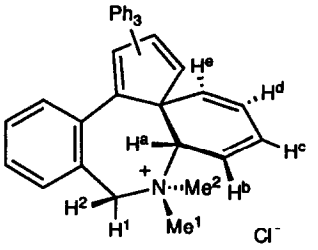


Compound **9** is only moderately stable, it rearranges in solution to yield the HCl adduct of **4a**. In methanol, in the presence of a base such as K_2CO_3, a different rearrangement occurs affording quantitatively and almost instantaneously the neutral compound **10**. The most striking feature of the ^1H NMR spectrum of **10** is that the

1,3-diene unit is still present and that the CH_2NMe_2 unit is no longer diastereotopic. The CH_2 resonates at a rather high field (2.71 ppm) compared to the other compounds described in this study.

Figure 1: NOE ^1H NMR observations of compound **9**

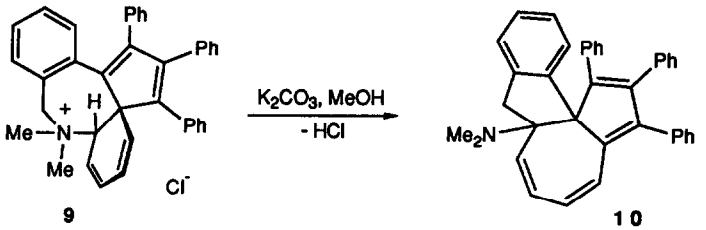
Irradiated ^1H	observed NOE
H^a	H^b (5.4%), Me^1 (0.5%), H^2 (2.5%)
H^b	H^a (2.7%), H^c (6.5%), Me^1 (2.7%)
Me^1	Me^2 (1.0%), H^a (3.6%), H^b (6.2%), H^1(2.4%)
Me^2	Me^1 (0.7%), H^e (3.2%), H^d (2.5%), H^c (1.9%)



9

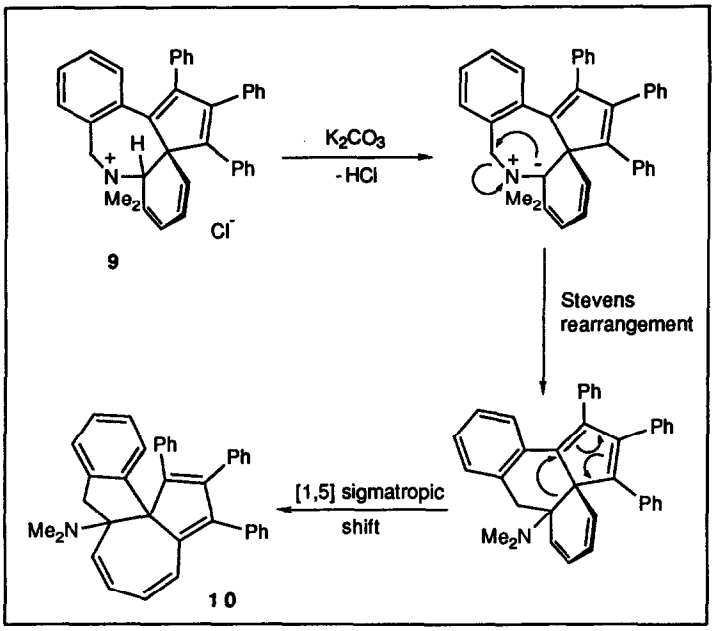
Compound **10** was fully characterised by a single crystal structure determination. An ORTEP diagram is presented in Figure 2. It shows that **10** is the result of a dramatic rearrangement of the precursor **9**. Thus, formally there has been insertion of the sp^3 carbon atom of the cyclohexadienyl unit into the C-N bond which occured concomitant with a C-C bond migration on the carbon α to the former orthometallated aryl ring, leading to a seven-membered carbocyclic ring. Related formation of [5.3.0] bicyclodecanes obtained *via* ring expansion of aryl groups have been described recently by *Heck* [8] and *Housecroft* et al.[16].

Equation 7:



9 **10**

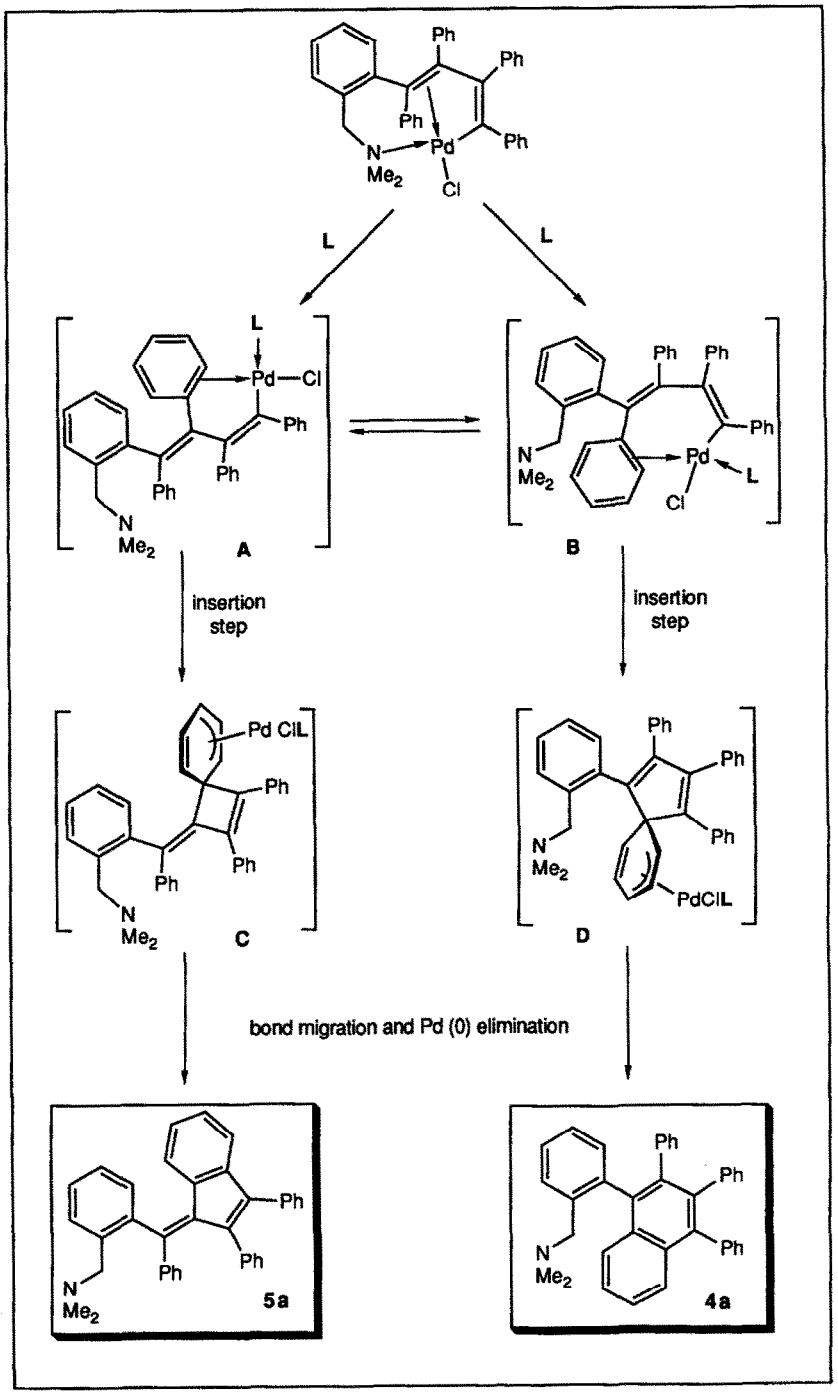
A possible reaction path for the formation of **10** is presented in Scheme 1. We propose that in the presence of a strong base, the proton at the tertiary carbon is removed affording the corresponding nitrogen-ylide intermediate. A Stevens rearrangment can then take place followed by a [1,5] sigmatropic shift.[18]



Scheme 1: Base induced intramolecular rearrangement of compound **9**

The structure determination of **10** provides futher evidence for the geometry of **9**, since the existence of the five-membered ring C1-C5 in **10** is a direct proof that **9** is formed *via* Pd-induced C-C bond formation between the vinylic unit in **3a** and the *ipso* carbon atom of the phenyl δ to palladium on the butadienyl chain.

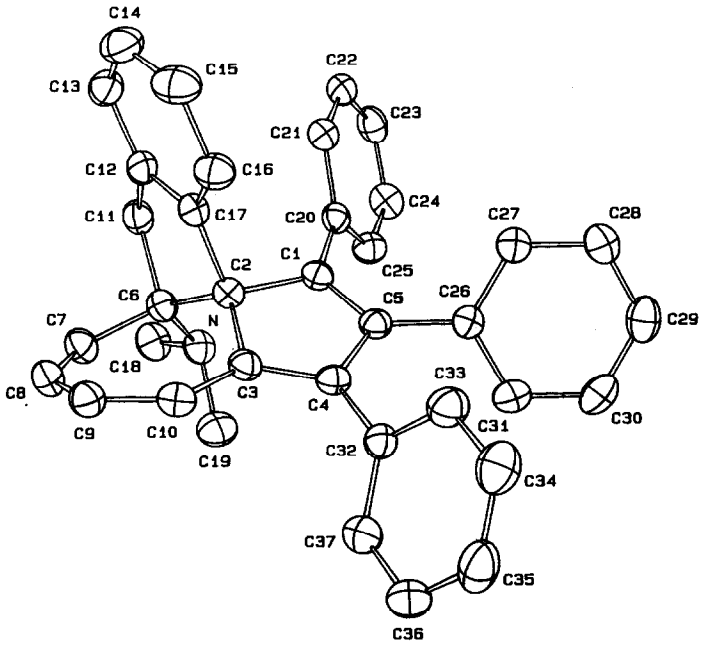
As for previous studies in our group, it appears that the annulation reaction of aryl rings occurs *via* spirocyclic compounds η^3-bound to palladium. Compound **9** is the result of the intramolecular nucleophilic addition of the NMe_2 group onto the η^3-allylic unit[19] of **D** (see Scheme 2), induced by the presence of triphenylphosphine. This peculiar behavior could be due to extra stabilisation of the spirocyclic intermediate in the presence of this ligand, which allows the formation of the C-N bond. We suggest that the reaction path depicted in Scheme 2 can be invoked for the formation of either naphthyl or fulvene units. A prerequisite for the rearrangments to take place is, obviously, a lowering of the chelate effect of the organic ligand in the starting compounds **3** or **6**. This could occur *via* cleavage of the N→Pd donative bond facilitated by the presence of excess ligand, L, such as maleic anhydride, pyridine or PPh_3. The butadienyl chain which is η^3-bound to palladium in the starting material can thus lead to other polyene systems (see **A** and **B**, Scheme 2) η^3-bound to Pd: *i.e.* hexatrienyl species which are formed by η^2-coordination of the aryl rings δ or γ to the Pd. A driving force for the occurrence of this new type of interaction with palladium could be a relief of the tension in **3** within the butadienyl unit η^3-bound to Pd. A few examples of organometallic molecules in which phenyl groups are in similar η^2-interaction with transition metals have been characterized by X-ray diffraction methods.[20] The next step could be assimilated to the intramolecular insertion of a cyclic C-C double bond into a Pd-C σ-bond[21] affording the key spirocyclic intermediates. Migration of one C-C bond together with 1,4-elimination of Pd then gives the final annulated products.



Scheme 2: Proposed mechanism for the annulation reactions

In order to explain the results observed it must be assumed that the formation of the spirocyclic intermediates is under thermodynamic control. The formation of the less strained spiro [4,5] decatetraenyl unit, **D**, should be favoured over that of **C**. Evidence for this is provided by the fact is that the naphthyl derivatives, **4**, are preferentially obtained under mild conditions, *e.g.* in refluxing MeOH in the presence of PPh_3.

Figure 2: ORTEP view of compound **10**



CONCLUSION

This study has provided new insight into the likely mechanism for the annulation of an aryl ring by intramolecular C-C coupling on the carbon *ortho* of that aryl ring. Previous studies in this field suggested alternative possibilities such as palladium induced C-H activation at that ortho position.[3b, 5b, 6] We believe that the obtained evidence from our studies shows that this latter pathway is less likely and that *ipso* intramolecular addition to provide spirocyclic intermediates is a more likely hypothesis.

EXPERIMENTAL

Unless stated otherwise, reactions were run in air. The solvents were dried appropriately and distilled prior to use. Pyridine was distilled twice over BaO and stored under N_2 on molecular sieves. Chromatographic separation of the products was carried out on silica or aluminium oxide (activity II-III) [Merck 70-230 mesh]. Analyses were performed by the Service d'analyses du CNRS, Strasbourg. ^1H and ^{13}C (^1H decoupled) NMR spectra were run with a Bruker SY200 spectrometer in $CDCl_3$ with TMS as internal standard, δ are given in ppm and J in Hz. Mass spectra of compounds were measured on a V6 ZAB-HF (FAB) spectrometer by the

Laboratoire de Spectroscopie de Masse (Strasbourg). The reagents were obtained commercially and used without purification. Compounds **1b-c**[22], **2**[23] and **3a**[10a] were synthesized by literature methods.

Compound **3b**: Diphenylacetylene (1.0 g, 5.65 mmol) was added to a stirred solution of **1b** (0.84 g,1.31 mmol) in CH_2Cl_2 (50 mL). The resulting mixture was stirred for 24 hr. at RT after which the red brown solution was filtered through a short celite plug to remove traces of metallic Pd. The solvent was removed in vacuo and the residue was stirred with cold pentane for 6 hr. The yellow suspension was filtered and the product washed with 3x25 mL pentane. After drying in vacuo the yield was 1.54 g (87 %) of **3b**. Analytically pure **3b** was obtained by quantitative precipitation from a CH_2Cl_2 / hexane mixture at -20° C.
Anal. calcd. for $C_{39}H_{35}Cl_3NO_2Pd$ (**3b** + $1CH_2Cl_2$): C, 61.43; H, 4.63; N, 1.83. Found: C, 61.53; H, 4.43; N, 1.90.
^{1}H NMR: 7.23-6.86 (m, 19H, Ar); 6.77 and 6.39 (2s, 2H, Ar); 6.55 (d, 2H, Ar); 6.00 (d, 2H, OCH_2O); 2.75 and 2.55 (2d, 2H, CH_2N, $^2J_{HH}$ =13.5); 2.72 and 2.37 (2s, 6H, NMe_2).

Compound **3c**: A procedure identical to that used for **3b**, starting with 1c afforded **3c** with similar yields.
Anal. calcd. for $C_{38.75}H_{35.5}Cl_{2.5}NPd$ (**3c** + 0.75 CH_2Cl_2): C, 65.52; H, 5.04; N, 1.97. Found: C, 65.52; H, 5.08; N, 1.80.
^{1}H NMR: 7.24-6.65 (m, 23H, Ar); 2.78 and 2.67 (2d, 2H, CH_2N, $^2J_{HH}$ =13.6); 2.73, 2.35 and 2.26 (3s, 9H, 3 Me).

Compound **4a**: A solution of **3a** (0.3 g, 0.47 mmol) in 10 mL of pyridine was stirred for 15 min at RT, and subsequently heated at reflux temperature for 6 h. The solvent was then removed under reduced pressure and the residue was dried in vacuo in order to remove all traces of pyridine. The reaction mixture was washed with 10 mL of ice-cold hexane and the product extracted with 50 mL of methylene chloride. The extract was filtered through a celite plug to remove the metallic palladium. The resulting orange-yellow filtrate was chromatographed on a silica gel column. Elution with methylene chloride removed unchanged starting material and impurities. The product was eluted with acetone to give a deep yellow fraction. (Elution with MeOH yielded oligomerisation and other products, this fraction was discarded). After drying on Na_2SO_4 and evaporation of acetone, the oily product was dissolved in ca. 2 mL of pentane. Compound **4a** (61 mg, 26%) was obtained as large off-white crystals by slow evaporation of this solution.
Melting point: 113°-115°C.
Anal. Calcd. for $C_{38.5}H_{34}NO_{0.5}$ (**4a** + 0.5 Me_2C=O): C, 88.35; H, 6.50; N, 2.68. Found: C, 88.7; H, 6.9; N, 2.7.
^{1}H NMR: 7.67-6.75 (m, 20H, Ar); 3.13 and 3.03 (2d, 2H, CH_2, $^2J_{HH}$ =13.5); 2.06 (s, 6H, 2 CH_3).
^{13}C NMR: 143-127 (m); 126.1; 125.8; 123.0; 120.6 (arom. C); 57.9 (CH_2-N); 43.2 ($N(CH_3)_2$).
M.S.: calcd. for $C_{37}H_{31}N$ = 489. m/z = 490 ($M+H^+$)

Compounds **4b** and **5b**: A solution of **3b** (0.70 g, 1.03 mmol) and 0.2 g of maleic anhydride in 50 mL of chlorobenzene was stirred for 30 min. at reflux temperature. The solvent was then evaporated under reduced pressure and the residue was dried in vacuo. The product was extracted with a 50 mL portion of CH_2Cl_2 and filtered through a celite plug in order to remove the palladium metal. The filtrate was concentrated to ca. 5ml and

chromatographed on a silica gel column. Elution with CH_2Cl_2 removed unchanged starting material and impurities. The product was eluted with CH_2Cl_2/acetone (1:3). After evaporation of the solvent, a mixture of **4b** and **5b** was obtained in a 4:1 ratio. Pure **4b** was obtained via fractional crystallization fron THF/pentane at -20°C. **5b** was not isolated.The yield of **4b** as pale yellow crystals was 0.21 g (38%).
Anal. calcd. for $C_{38}H_{32}NO_2$ C, 85.36; H, 6.03; N, 2.62. Found: C, 85.18; H, 5.93; N, 2.59.
^{1}H NMR of free-base **4b**: 7.68-7.10; 6.95-6.75 (2m, 19 H, Ar), 7.03 and 6.69 (2s, 2H, Ar), 5.94 (d, 2H, OCH_2O), 3.02 and 2.90 (2d, 2H, CH_2N, $^2J_{HH}$ = 14.2), 2.05 (s, 6H, 2 CH_3) **5b**: 6.05 (d, 2 H, CH_2O_2), 3.28 and 3.18 (2d, 2 H, NCH_2, $^2J_{HH}$ = 13.9), 2.03 (s, 6 H, NMe_2). ^{1}H NMR of **4b**-HBF_4: 7.7-6.6 (m, 21H, Ar), 6.05 (d, 2H, OCH_2O), 3.66 and 3.54 (2d, 2H, CH_2N, $^2J_{HH}$ = 14.3), 2.73 (d, 3H, CH3, $^3J_{HH}$ = 4.7), 2.43 (d, 3H, CH_3).

Compounds **4c** and **5c**: To a solution of **3c** (2.35 g, 3.63 mmol) in 50 mL chlorobenzene was added maleic anhydride (0.5 g). The resulting mixture was kept at reflux temperature for 1 hr. after which the solvent was removed under reduced pressure. The residue was extracted with 2 x 50 mL of dichloromethane and the combined extracts were filtered on a short celite column to remove the palladium metal. The orange red filtrate was concentrated and chromatographed on a silica column. Elution with CH_2Cl_2 eliminated unchanged **3c** and impurities, while a 1:1 mixture of CH_2Cl_2/acetone eluted the product. After removal of the solvent, the orange residue was dissolved in MeOH (25 mL) and excess K_2CO_3 was added. After 6 hr. stirring the solvent was removed under reduced pressure and the product was extracted with CH_2Cl_2. The ^{1}H NMR spectrum showed that **4c** and **5c** were present in a 3:1 ratio. A mixture of **4c** and **5c** (10:1 ratio) was obtained via fractional crystallization from Et_2O/pentane to yield 411 mg (23%) of orange micro-crystals.
Anal. calcd. for $C_{38}H_{33}N$: C, 90.61; H, 6.60; N, 2.78. Found: C, 90.64; H, 6.62; N, 2.96.
^{1}H NMR: **4c**: 7.75-6.64 (m, 22 H, Ar), 3.07 and 2.99 (2d, 2 H, CH_2, $^2J_{HH}$ = 14), 2.09 (s, 3 H, CH_3), 1.95 (s, 6H, $N(CH_3)_2$). **5c**: 7.57-6.74 (m, 21 H, Ar), 6.20 (d, 1 H, Ar, $^3J_{HH}$ = 7.8), 3.30 and 3.20 (2d, 2 H, NCH_2, $^2J_{HH}$ = 13.6), 2.37 (s, 3H, CH_3), 2.02 (s, 6H, NMe_2).

Compound **6**: A solution of **2** (230 mg; 0.3 mmol) and diphenylacetylene (216 mg; 1.2 mmol) in CH_2Cl_2 (30 mL) was stirred at room temperature for 5 hr. The solution was then reduced to 5-10 mL and chromatographed on silica gel (10x2.5 cm column; CH_2Cl_2): elution with CH_2Cl_2 afforded an orange solution to yield **6** (430 mg; 97%).
Anal. Calcd. for $C_{41}H_{36}NClFePd$: C, 66.51; H, 4.90; N, 1.89; found: C, 66.60; H, 5.03; N, 1.88.
^{1}H NMR: 7.56; 7.10; 6.85; 6.66; 6.56 (5m; 20 H; 4 Ph), 4.36; 4.33; 3.96 (3m; 3 H; C_5H_3), 3.96 (s; 5 H; C_5H_5), 3.08; 2.50 (2s; 6 H; NMe_2), 2.26; 1.68 (2d; 2 H; CH_2N; $^2J_{HH}$ = 14.3).
^{13}C NMR: 47.7; 52.4 (2s; NMe_2), 59.5 (CH_2), 67.3; 68.1; 83.9; 86.5 (C_5H_3), 71.0 (C_5H_5), 88.4; 111.8 (C=C), 126.0-128.0 (m), 131.2; 135.1; 138.1; 140.2; 146.0; 149.3 (Ar).

Compound **7**: (This reaction was preformed under N_2). A suspension of **6** (660 mg; 0.89 mmol) and triphenylphosphine (933 mg; 3.56 mmol) in methanol (25 mL) was stirred at room temperature. A yellow precipitate was formed. After 1h, the reaction mixture was filtered and the solution was evaporated to dryness vacuum. The orange residue was dissolved in CH_2Cl_2 (10 mL) and Na_2CO_3 was added. After filtration the solution was reduced to 3-5 mL and chromatographed on alumina [15x2.5 cm column]. The column was eluted

first with a hexane-Et_2O (9/1) solution (100 mL); elution with pure Et_2O afforded an orange solution to yield **7** (500 mg; 94%).
Anal. Calcd. for $C_{41}H_{35}NFe$: C, 82.40; H, 5.90; N, 2.34; found: C,82.29; H, 6.25; N, 2.38.
^1H NMR: 10.16 (d, 1H, Ar, $^3J_{HH}$ = 8.6),7.67-6.48 (m, 18H, Ar), 4.49, 3.85 and 3.72 (3m, 3H, C_5H_3), 4.19 (s, 5H, C_5H_5), 3.65 and 3.08 (2d, 2H, NCH_2, $^2J_{HH}$ = 13.7), 2.22 (s, 6H, NMe_2).
^{13}C NMR: 142.5, 142.2, 140.9, 139.9, 138.9, 138.4 (Ar), 132.3-131 (Ar), 129.1, 128.6, 128.4, 127.7, 127.1 (Ar), 126.4 (m, Ar),125.6, 125.1, 123.7 (Ar), 70.0 (C_5H_5), 87.6, 86.2, 71.9, 69.1, 65.1 (C_5H_3), 58.2 (s, CH_2), 45.9 (NMe_2).

Compound **8**: A solution of compound **7** (150 mg; 0.25 mmol) and MeI (16 µL; 0.25 mmol) in acetone (10 mL) was stirred at room temperature for 1h. After removal of the solvent under vaccum, the residue was dissolved in chlorobenzene (10 mL) and heated at reflux temperature. After 30 min, the solvent was removed under vacuum, the reaction mixture dissolved in CH_2Cl_2 and chromatographed on silica gel [10x2 cm column; pentane]. Elution with a pentane-CH_2Cl_2 (7/3) mixture afforded an orange solution of **8** (105 mg; 76%).
Anal. Calcd. for ($C_{39}H_{28}Fe$ + 0.5 C_6H_6): C, 85.28; H, 5.28; found: C, 85.39; H, 5.24.
^1H NMR: 9.98 (d, 1H, Ar, $^3J_{HH}$ = 8.5), 7.70-6.51 (m, 17H, Ar), 4.73, 4.23 (2m, 2H, C_5H_3), 4.21 (s, 6H, C_5H_5 + C_5H_3), 3.92 and 3.54 (2d, 2H, CH_2, $^2J_{HH}$ = 12.6).
^{13}C NMR: 144.5 and 142.1 (Ar), 140.0-124.0 (m, Ar), 70.2 (C_5H_5), 91.5, 81.6, 74.3, 67.7, 64.8 (C_5H_3), 35.0 (CH_2).

Compounds **9a** and **4a**: (This reaction was performed under N_2). A mixture of **3a** (632 mg; 1 mmol) and PPh_3 (1.05 g; 4 mmol) in MeOH (30 mL) was refluxed for 90 min. The suspension was cooled and filtered, after which the solvent was removed in vacuo and the residue extracted with MeOH (15 mL). The methanol solution was evaporated and the orange residue dissolved in CH_2Cl_2 (15 mL). K_2CO_3 (1 g) was added. After 15 min stirring, the solution was filtered and reduced to 5 mL and hexane (50 mL) was added, **9a** precipited as a beige solid. The remaining yellow solution was concentrated and chromatographed on alumina [10x2.5 cm column, CH_2Cl_2]. Elution with a CH_2Cl_2-Et_2O (9/1) mixture afforded an yellow solution to yield **4a** (200 mg; 40%).
For a futher purification, **9a** was extracted with a H_2O/MeOH (1/1) solution (10 mL) and filtered. The solvent was removed under vacuum, the residue dissolved in CH_2Cl_2 (5 mL) and **9a** precipited as a white solid (120 mg; 23%) by addition of hexane.
^1H NMR: **9a**: (see Figure 1 for the labelling of some atoms) 8.16 (d, 1H, Ar, $^3J_{HH}$ = 7.3), 7.35-6.78 (m, 17H, Ar), 6.72 (d, 1H, Ar, $^3J_{HH}$ = 7.0), 6.31 (dd, 1H, H_d, $^3J_{HcHd}$ = 5.4), 6.0 (dd, 1H, H_c), 5.82 (d, 1H, H_e, $^3J_{HdHe}$ = 9.3), 5.72 and 5.12 (2d, 2H, CH_2N, $^2J_{HH}$ = 12.5), 5.43 (dd, 1H, H_b, $^3J_{HbHc}$ = 9.6), 4.37 (d, 1H, H_a, $^3J_{HaHb}$ = 4.9), 3.74 and 2.94 (2s, 6H, NMe_2).
M.S.: calcd. for $C_{37}H_{32}N$ = 490: m/z = 490 (M^+), 489 (M^+ - H), 475 (M^+ - Me), 446 (M^+ - NMe_2)

Compound **10**: (This reaction was carried out under N_2). A mixture of **3a** (1.90 g; 3 mmol) and PPh_3 (3.15 g; 12 mmol) in MeOH (50 mL) was refluxed for 90 min. The resulting suspension was cooled and filtered. K_2CO_3 (1g) was added to the filtrate which produced a colour change from orange to yellow. After filtration, the solvent was removed in vacuo and the residue extracted with Et_2O (50 mL). The solution was then concentrated and

chromatographed on alumina [15 x 2.5 cm column; Hexane-Et_2O (9/1)]. A yellow fraction moved rapidly down the column to yield **10** (450 mg; Y = 30%). Elution with pure Et_2O afforded an orange solution of **4a**.
Anal. Calcd. for ($C_{37}H_{31}N$): C, 90.79; H, 6.34; N, 2.86; found: C, 91.3; H, 6.6; N, 2.9.
Melting point (°C): 184-5 (crystallised from an Et_2O-Hexane solution).
^1H NMR: 7.27-6.66 (m, 19H, Ar), 6.35 (d, 1H, H_aC=, $^3J_{HaHb}$ = 11.25), 5.83 (dd, 1H, H_cC=, $^3J_{HbHc}$ = 7.5), 5.61 (dd, 1H, H_bC=), 5.36 (d, 1H, H_dC=, $^3J_{HdHc}$ = 12.53), 2.70 (s, 2H, CH_2), 2.32 (s, 6H, NMe_2).
^{13}C NMR: 151.6, 147.4, 145.7, 144.2, 143.0, 140.8, 138.3, 135.5, 135.2 (9s), 130.2-125.9 (m), 130.0(s, H_dC=), 127.3 (s, H_aC=), 126.6 (s, H_cC=), 124.5, 123.5 (s, H_bC=), 122.0, 46.0 (s, CH_2), 41.0 ($N(CH_3)_2$).

X-ray structure determination of compound **10**:[24] $C_{37}H_{31}N$, mol. weight = 489.7 monoclinic, $P2_1/n$, a = 9.402(3) Å, b = 23.215(7) Å, c = 12.348(4) Å, β = 95.37(2)°, V = 2683 $Å^3$, Z = 4, D(calcd) = 1,212 $g.cm^{-3}$, λ(Cu Kα) = 1.5418 Å (graphite monochromator), T = -100°C. A Philips PW1100/16 diffractometer, equipped with local-built low temperature device, was used to collect 3026 reflections ($3° < 2\theta < 50°$) on a yellow crystal (0.20 x 0.30 x 0.34 mm). Of these, 2341 were observed [$I > 3\sigma(I)$]. Empirical absorption corrections and Lorentz and polarization corrections were applied to the data. All non-hydrogen atoms were located by direct methods, and they were refined anisotropically. The hydrogen atoms were included as idealized contributions. R = 0.030, Rω = 0.052, GOF = 1.203, final residual = 0.09 $eÅ^{-3}$. All computations used MOLEN on a VAX computer.[25]

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