JOM 23437

Palladation and subsequent functionalization at the second *peri* position of 1-substituted naphthyl groups

Michel Pfeffer [a], Nohma Sutter-Beydoun [a], André De Cian [b] and Jean Fischer [b]

[a] *Laboratoire de Synthèses Métalloinduites, Unité associée au CNRS no. 416, Université Louis Pasteur, 4, Rue Blaise Pascal, 67070 Strasbourg Cedex (France)*

[b] *Laboratoire de Cristallochimie et de Chimie Structurale, URA 424 du CNRS, Université Louis Pasteur, 4, Rue Blaise Pascal, 67070 Strasbourg Cédex (France)*

(Received September 11, 1992)

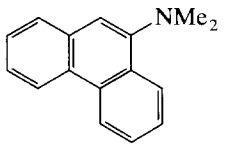
Abstract

The cyclopalladation of ligands having a naphthyl group substituted at the 1-position by either amino or imino units has been studied. Palladation of the naphthyl unit occurs as expected at the second *peri* position of the *N,N*-dialkylamino substituted derivatives. However, the imines were not palladated at the 8-position of the naphthyl unit. The last ligands were synthesized by condensation of either acetone or acetophone on Pd(1-aminonaphthalene)$_2$Cl$_2$. In the case of the acetone derivative, this afforded a Pd complex having two imines N-coordinated to the metal; the compound obtained with acetophenone did lead to a cyclopalladation product, but the metallation occurred at the *ortho* position of the phenyl group of the acetophenone unit rather than on the 8-position of the 1-iminonaphthalene. The cyclopalladated compounds obtained with the 1-*N,N*-dialkylaminonaphthalenyl ligands afforded reasonable yields of *N*-alkylquinolines through reaction with internal alkynes such as tolane, dimethylacetylenedicarboxylate, and ethyl-3-phenylpropynoate. Thus, starting with the cyclopalladated 9-dimethylaminophenanthrene, good yields of aporphine precursors can be obtained.

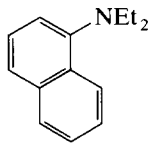
1. Introduction

Cyclopalladated compounds, derived from intramolecular metallation of N-containing ligands, can provide new synthetic pathways to heterocyclic compounds by reaction with internal alkynes [1]. Among the various reagents that our group [1a], and others [1b], have so far studied to this purpose, 1-dimethylaminonaphthalene proved to be of special interest and it was shown that heterocycles could be obtained with a large variety of alkynes. Moreover, using an iodide derivative of 1-dimethylaminonaphthalene, a catalytic system was developed by which the desired heterocycles could be obtained in reasonable to good yields [2].

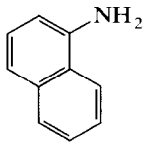
We have therefore investigated whether 9-dimethylaminophenanthrene (**1a**) or other reagents (**1b–1f**) containing a naphthyl group substituted at the 1-position by different amine or imine functions, might be palladated at the second *peri* position, in order to check the scope of the reactions of the resulting cyclopalladated compounds with alkynes.



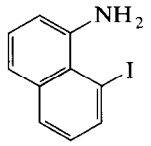
(**1a**)



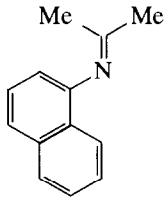
(**1b**)



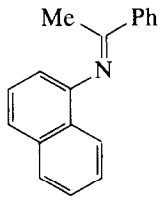
(**1c**)



(**1d**)



(**1e**)



(**1f**)

Correspondence to: Dr. M. Pfeffer.

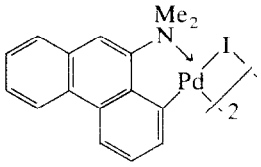
0022-328X/93/$6.00

2. Results and discussion

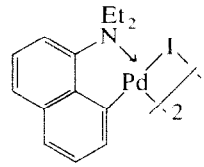
2.1. Palladation of the ligands 1a–1f

Palladation of 9-(dimethylamino)phenanthrene (**1a**) with $Pd(OAc)_2$ affords good yields of the expected acetato-bridged dimer having the palladium atom at the 8-position. Compound **2** was obtained quantitatively by treating the latter with an excess of NaI in MeOH.

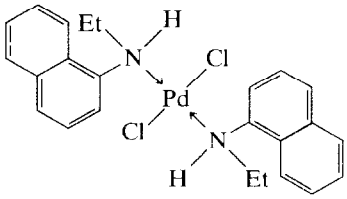
The substitution of methyl by ethyl groups would seem *a priori* to be a trivial modification as far as the metallation of 1-dialkylaminonaphthalenes by Pd^{II} is concerned. However, we found that this slight change dramatically reduced the ease of palladation at the 8-position of the naphthyl ring. We found that the best yields (*ca.* 30%) of **3** were obtained when using $[PdCl_2(PhCN)_2]$ as the metallating agent in methanol, followed by treatment *in situ* with an excess of NaI. It is noteworthy that most (70%) of the palladium containing compound is an ill-defined orange material, soluble in MeOH and in CH_2Cl_2. All other palladium sources led to lower yields of **3**. For instance with $Li_2[PdCl_4]$, the reaction led to significant formation of metallic palladium, but **4** could be isolated from the reaction mixture. Its structure was deduced from analytical, IR and ^1H NMR data. The formation of this product seems to be akin to related results from this laboratory; a similar dealkylation of a tertiary arylamine takes place in the presence of $Li_2[PdCl_4]$ in MeOH [3].



(2)



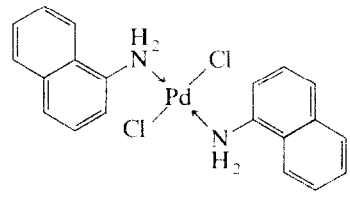
(3)



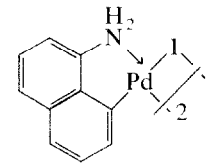
(4)

Compound **3** is soluble in CH_2Cl_2 and in $CHCl_3$ but its ^1H NMR spectrum shows a better resolution in the presence of a small amount of pyridine-d_5 (which obviously affords the corresponding mononuclear species). The signals of the CH_2 protons appear as an ABX_3 pattern both in the presence and in the absence of pyridine (Py). This can be rationalized by assuming that the CH_2 units are not in the molecular symmetry plane; they therefore lack C_2 symmetry and, as a consequence, are diastereotopic. (We wish to thank one of the referees for having helped clarify this.)

The addition of 1-aminonaphthalene (**1c**) to $[PdCl_2(PhCN)_2]$, $PdCl_2$, or $Li_2[PdCl_4]$ in methanol quantitatively afforded **5** for which we could not obtain any ^1H NMR data because of its insolubility. In the presence of pyridine, **5** leads immediately and quantitatively to $[PdPy_2Cl_2]$. This suggests the formulation of **5** depicted below, in which the *N*-ligand is coordinated simply to Pd *via* the nitrogen lone pair. However, the desired cyclopalladated derivative **6** could be obtained in good yield *via* the oxidative addition of 1-iodo-8-aminonaphthalene (**1d**) to $Pd(dba)_2$, according to the method described by Clark and Dyke [5].



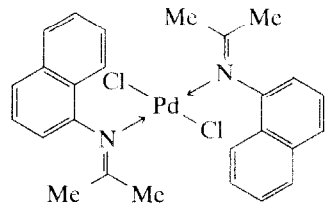
(5)



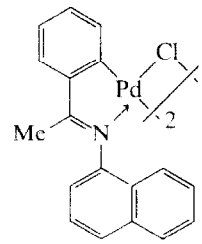
(6)

The ^1H NMR spectrum of di(μ-iodo)bis(8-amino-1-naphthyl-*C*,*N*)dipalladium (**6**) could also only be observed in the presence of pyridine because of the poor solubility of the dimer.

The failure to palladate the naphthyl unit of 1-aminonaphthalene is not surprising, since it is well established that the palladation of aryl units of primary amines is rather difficult to achieve. This has only previously been observed in the case of triphenylmethylamine [6] and benzylamine [7]. However, it has very often been shown that the palladation of imines occurs very readily. We did not succeed in obtaining the free 1-iminonaphthalene derivatives **1e** and **1f**, the imine function of these compounds being very prone to hydrolysis. However, we found that their synthesis within the coordination sphere of palladium could be easily achieved by treating compound **5** in refluxing acetone or acetophenone [8]. These reactions afforded good yields of **7** and **8**, respectively.



(7)



(8)

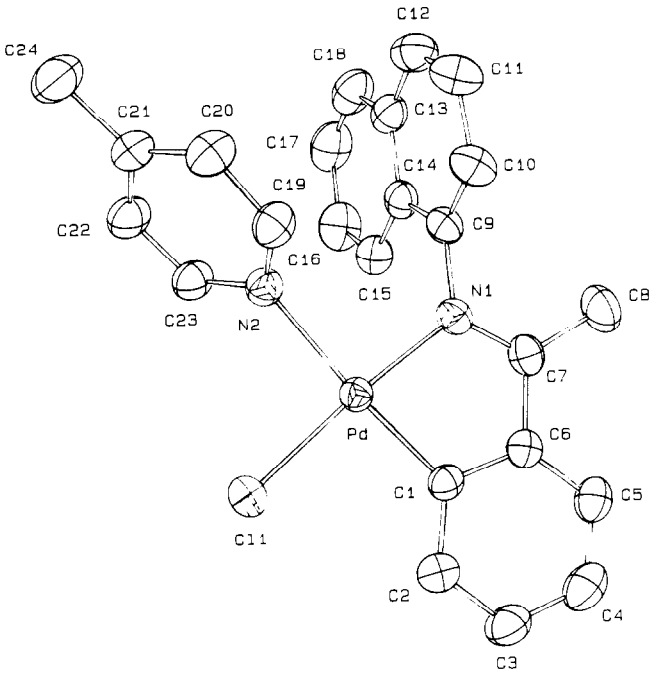


Fig. 1. ORTEP view of compound **9**. Ellipsoids are scaled to include 30% of electronic density; H atoms are omitted for clarity.

The ^{1}H NMR spectrum of non-cyclopalladated compound **7** reveals that the four methyl groups are inequivalent. Two methyl groups resonate at rather lower field (3.42 and 3.08 ppm) than the others, 1.71 and 1.72 ppm. This behaviour, together with the coalescence of the signals which occurs above 30°C, is reminiscent of that of related compounds having two hydrazones coordinated to Pd [9]. The non-equivalence of the methyl groups that resonate at lower field might be rationalized by assuming that one of the methyls (3.42 ppm) experiences a deshielding by the Pd atom.

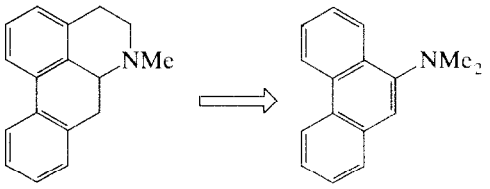
Analysis of the cyclometallated compound **8** showed it to be a 1:1 adduct of the new imine and its insolubility suggests a chloride-bridged dimer. In the presence of 4-MeC_5H_4N a palladium mononuclear compound **9** was obtained whose characterization was much easier. Its structure was established via an X-ray diffraction study. The ORTEP diagram of **9** is presented in Fig. 1. It is immediately apparent that **9** is indeed a cyclopalladated derivative, however, the Pd–C bond has not been formed as expected (see the discussion below) at the 8-position of the naphthyl group but on the *ortho* position of the phenyl ring of the acetophenone unit. The bond distances and angles within the molecule are consistent with what is usually found for this type of compound. The most surprising feature of the structure of **9** is that the 4-methyl pyridine ligand is coordinated to Pd *trans* to the carbon atom σ-bonded to Pd. Usually in this type of mononuclear compound, the pyridine is found *trans* to the nitrogen atom of the cyclopalladated ligand [10]. Morever, in the present case, it seems that the position *trans* to C1 is much more sterically hindered than the position *trans* to N1.

The ^{1}H NMR spectrum of **9** clearly indicates that it is a 1:4 mixture of two isomers. It is well established that a pyridine *cis*-coordinated to a σ-bonded aryl ring of a cyclopalladated unit results in a high-field shift of the proton *ortho* to the palladated carbon atom, due to the shielding effect of the pyridine [11]. Thus the minor isomer having an *ortho* proton resonating at 6.39 ppm must be that having the 4-MeC_5H_4N *cis* to the Pd–C bond. The two isomers of **9** should be the result of an equilibrium in which the 4-methyl pyridine ligand migrates from the *trans* to the *cis* position of the carbon σ-bonded to Pd. This equilibrium should be attained quickly, since the ^{1}H NMR spectrum of a solution of a single crystal of **9** (identical to that used for the X-ray structure analysis) displayed exactly the same features. We were not able to monitor the isomerization of **9** with increasing the temperature because it was not possible to dissolve the crystal quickly enough at *ca.* −80°C. We have recently reported a similar behaviour for a related Pd complex which was present in solution as two isomers whereas only one (the thermodynamically most stable) was found in the solid state [12].

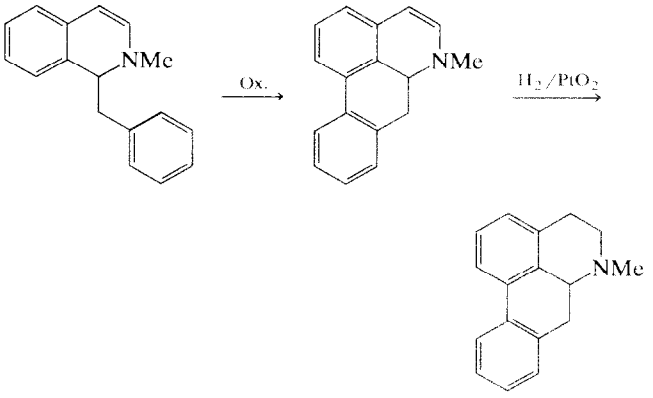
The palladation of the aryl rather than the naphthyl group in **8** is somehow surprising, as one would assume that the compound resulting from the palladation of the latter would be more stable than the one obtained by the *ortho*-metallation of the former. A possible explanation for this behaviour is the conformation of the ligand which is such that it prevents the proton at the 8-position of the naphthyl ring from interacting with the palladium atom. This is visible in compound **7**, for which we know (see above) from the ^{1}H NMR data that one methyl group interacts with the Pd atom, and therefore this is no longer possible for the second *peri* C–H unit of the naphthyl group. We have confirmed that **7** is very resistant to palladation at this position. Neither prolonged heating in toluene nor treatment with a base such as NaOAc were successful. We have also abstracted the chloride ions in **7** with $AgBF_4$ in order to remove steric restrictions which might allow the necessary conformational change prior to metallation but this did not lead to the desired palladation reaction. This result is in line with related observations in our laboratory [13].

2.2. *Reaction of the compounds 2, 3 and 6 with alkynes*

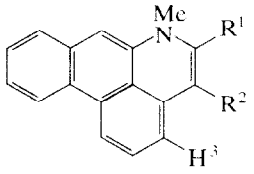
These reactions are interesting because they may lead to novel routes towards aporphine derivatives, according to the following scheme:



Several syntheses for these important biologically active compounds are known, but most of them include modifications of isoquinoline units which are already present [14]. An example of such a procedure is given below.

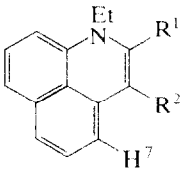


No clean reaction was observed when treating **6** with either diphenylacetylene, dimethylacetylene dicarboxylate, or ethyl-3-phenylpropyonate. This afforded a complicated mixture of products none of which could be characterized. On the other hand, **2** and **3** reacted with the same type of alkyne to afford the expected heterocyclic compounds **10** and **11**, respectively.



10a: $R^1 = CO_2Et$, $R^2 = Ph$

10b: $R^1 = R^2 = CO_2Me$



11a: $R^1 = R^2 = Ph$

11b: $R^1 = CO_2Et$, $R^2 = Ph$

The yield of **10b** was rather low because its formation was competitive with the alkyne trimerization. The yields of the other compounds, **10a**, **11a**, and **11b**, were reasonable. In the case of the reaction with ethyl-3-phenylpropyonate we confirmed that the reaction displayed a high degree of regioselectivity, since only one isomer could be found by ^1H NMR spectroscopy in each case. The regioselectivity is the same as in the other related heterocycles we have synthesized in that the phenyl group is found on the carbon atom attached to the nitrogen atom [2]. This is easily established from the ^1H NMR spectra of **10a** and **11b**, which showed the characteristic low field shifts of the protons H3 and H7, respectively.

We were able to check that the reaction of **3** with diphenylacetylene to produce **11a**, occurs with formation of ethylene iodide together with traces of ethylene, since these were detected experimentally in the gas phase as well as in the reaction mixture. Although we do not have any kinetic evidence, we propose that the dealkylation reaction of the nitrogen atom could be of the S_N2 type. However, this merits further investigation, since the dealkylation of tertiary amines seems to be quite rare in organic chemistry [15]. It would be particularly interesting to determine whether the palladium plays a role in this reaction.

The main conclusion that can be drawn from this study is that cyclopalladation *via* a C–H abstraction process of naphthalyl derivatives at a *peri* position seems to be limited to those species having a dialkyamino unit at the 1-position. Provided that 9-dimethylaminophenanthrene derivatives are used as starting materials, these organometallic compounds may be used as intermediates for easy access to functionalized aporphines. Further work is in progress to evaluate the synthetic potential of this new procedure.

3. Experimental details

^1H NMR spectra were recorded at 200.13 MHz using a Bruker SY200 instrument. Proton chemical shifts are positive downfield relative to external $SiMe_4$. Elemental analyses were carried out by the Service Central de Microanalyses du CNRS (France).

3.1. Syntheses

1-Diethylaminonaphthalene (**1b**) [16] and 1-amino-8-iodo naphthalene (**1d**) [17] were prepared according to published methods. All other reagents were obtained from commercial sources and were used as received without further purification.

3.1.1. Synthesis of 9-(Dimethylamino)phenanthrene (1a)

To a solution of 9-aminophenanthrene (3 g, 15.51 mmol) in CH_2Cl_2 (50 ml) was added a large excess of dimethyl sulphate (10.08 g, 80 mmol) and a catalytic amount of tetrabutylammonium bromide (0.249 g, 0.77 mmol) dissolved in water (50 ml). The mixture was left to stir for 6 days; a large excess of KOH (5.6 g, 100 mmol) was added and the mixture was stirred for a further 24 h. The organic layer was separated, evaporated, washed with water (100 ml) and dissolved in Et_2O (100 ml). This solution was dried with Na_2SO_4. After filtration and evaporation of the solvent, **1a** was

obtained as a white-pink solid (3.08 g, 90%). Anal. Found: C, 86.98; H, 6.82; N, 6.12. $C_{16}H_{15}N$ calcd.: C, 86.84; H, 6.83; N, 6.33%. ^1H NMR ($CDCl_3$): δ 8.78–7.54 (m, $8H_{arom}$); 7.27 (s, 1H, H^{10}); 2.95 (s, 6H, NCH_3).

3.1.2. Synthesis of compound 2

To a solution of palladium acetate (1.124 g, 5 mmol) in acetic acid (50 ml), was added **1a** (1.127 g, 5.1 mmol). The mixture was stirred for 24 h at 20°C. The acetate dimer was obtained as a white solid which precipitated out. This was filtered off, washed with pentane (100 ml) and taken up in methanol (50 ml) with an excess of sodium iodide. The colour turned yellow and the mixture was stirred for 4 h. After evaporation of the solvent, **2** was extracted with a mixture of CH_2Cl_2/MeCN (3:1) as an orange-yellow solid (2.082 g, 90%). Anal. Found: C, 41.87; H, 3.06; N, 3.14. $C_{32}H_{28}I_2N_2Pd_2$ calcd.: C, 42.34; H, 3.11; N, 3.09%. ^1H NMR ($CDCl_3 + C_5H_5N$-d_5): δ 8.62 (dd, 1H, $H^{1,4}$); 8.34 (d, 1H, H^5); 7.86 (dd, 1H, $H^{4,1}$); 7.67–7.50 (m, 3H, $H^2 + H^3 + H^{10}$); 7.24 (t, 1H, H^6); 5.92 (d, $1H_{arom}$, $^3J(HH) = 7.3$ Hz); 3.77 (s, 6H, NCH_3).

3.1.3. Synthesis of compound 3

To a solution of $[PdCl_2(PhCN)_2]$ (1.305 g, 3.40 mmol) in methanol (40 ml), was added dropwise a solution of **1b** (1.350 g, 6.8 mmol) in methanol (10 ml). After stirring for 1 h a brown-orange precipitate appeared. This was filtered, washed with methanol (50 ml) and taken up in acetone (50 ml) containing an excess of NaI. The system darkened instaneously. After evaporation of the solvent, the resulting solid was dissolved in dichloromethane then filtered on a silica-gel column (6 cm). After removal of the solvent and washing with pentane (100 ml), **3** was obtained as an orange solid (0.439 g, 30%). Anal. Found: C, 37.98; H, 3.57; N, 3.09. $C_{28}H_{32}I_2N_2Pd_2$ calcd: C, 38.96; H, 3.74; N, 3.24%. ^1H NMR ($CDCl_3 + C_5H_5N$-d_5): δ 7.26–6.97 (m, $5H_{arom}$); 5.74 (d, $1H_{arom}$, $^3J(HH) = 7.1$ Hz); 4.41 and 3.30 (2m, ABX_3 pattern, 4H, CH_2, $^2J(HH) = 11.8$ Hz); 1.39 (t, 6H, CH_3, $^3J(HH) = 6.9$ Hz).

3.1.4. Synthesis of compound 4

To a solution of $Li_2[PdCl_4]$ (1.616 g, 6.16 mmol) in methanol (100 ml), was added a solution of **1b** (2.44 g, 12.32 mmol) in methanol (10 ml). After stirring for 2 h a brown-green solid appeared. This was filtered off and **4** was obtained after extraction with dichloromethane (50 ml) as a green solid (0.217 g, 6.8%). Anal. Found: C, 52.25; H, 4.68; N, 5.07 (the amount of CH_2Cl_2 was confirmed by ^1H NMR spectroscopy. $C_{24}H_{26}Cl_2N_2$-Pd + 1/2 CH_2Cl_2 calcd.: C, 52.41; H, 4.81; N, 4.99%. ^1H NMR ($CDCl_3 + C_5H_5N$-d_5): δ 7.83–7.20 (m, $6H_{arom}$); 6.60 (d, $1H_{arom}$, $^3J(HH) = 7.4$ Hz); 4.27 (broad s, 1H, N–H); 3.31 (q, 2H, CH_2); 1.40 (t, 3H, CH_3, $^3J(HH) = 7.1$ Hz).

3.1.5. Synthesis of compound 5

To a solution of $[PdCl_2(PhCN)_2]$ (1.5 g, 3.91 mmol) in dichloromethane (50 ml) was added an excess of 1-aminonaphthalene (1.144 g, 8 mmol). After stirring for 15 min an orange precipitate appeared. Compound **5** was quantitatively obtained as an orange solid after filtration and washing with dichloromethane. Anal. Found: C, 50.22; H, 3.84; N, 5.75. $C_{20}H_{18}Cl_2N_2Pd$ + 1/4 CH_2Cl_2 calcd.: C, 50.20; H, 3.82; N, 5.78%.

3.1.6. Synthesis of compound 6

To a solution of $[Pd(dba)_2]$ (1.027 g, 1.8 mmol) in toluene (20 ml), was added a slight excess of 1-amino-8-iodonaphthalene ligand **1d** (0.528 g, 1.96 mmol) dissolved in toluene (20 ml). The mixture was stirred at 20°C for 1 h and the solution turned from purple to light brown and a brown precipitate appeared. This was filtered off and washed with pentane (50 ml) and **6** was obtained as a light brown solid (0.501 g, 74%). Because of its insolubility, **6** could not be recrystallized and therefore no good elemental analysis could be obtained. ^1H NMR ($CDCl_3 + C_5H_5N$-d_5): δ 7.62–7.06 (m, $5H_{arom}$); 5.97 (d, $1H_{arom}$, $^3J(HH) = 7.0$ Hz); 5.87 (s, 2H, NH_2).

3.1.7. Synthesis of compound 7

A suspension of **5** (0.462 g, 1 mmol) was heated under reflux in acetone (60 ml) for 3 h. The orange solution obtained was evaporated and the resulting solid dissolved in the minimum amount of dichloromethane. Addition of pentane (30 ml) gave **7** as an orange-yellow solid (0.492 g, 90%). Anal. Found: C, 56.42; H, 4.71; N, 5.04. $C_{26}H_{26}Cl_2N_2Pd$ calcd.: C, 57.42; H, 4.80; N, 5.15%. ^1H NMR ($CDCl_3$): δ 7.93–7.31 (m, $14H_{arom}$); 3.42, 3.09, 1.72 and 1.71 (4s, 12H, $4CH_3$).

3.1.8. Synthesis of compounds 8 and 9

A suspension of **5** (0.200 g, 0.43 mmol) in acetophenone (10 ml) was heated under reflux for 25 min. The dark orange solution obtained was evaporated to dryness under reduced pressure. The addition of a mixture of dichloromethane/hexane gave **8** as a green solid (0.134 g, 80%). This compound was only characterized as a mononuclear derivative; see **9**. To a suspension of **8** (0.100 g, 0.12 mmol) in dichloromethane (10 ml) was added an excess of 4-methylpyridine (0.093 g, 0.1 mmol). The solid dissolved instantly affording a dark green solution which was filtered off on a Celite column (4 cm). The solvent was evaporated and the resulting solid washed with 30 ml of pentane to elimi-

nate the excess of 4-methylpyridine and **9** was obtained quantitatively as a yellow solid. Anal. Found: C, 54.18; H, 4.03, N, 4.99. $C_{25}H_{23}Cl_3N_2Pd$ (**9** + CH_2Cl_2) calcd.: C, 53.23; H, 4.08; N, 4.97%. ^1H NMR ($CDCl_3$): δ 8.74–7.00 (m, $14H_{arom}$); 6.39 (d, $1H_{arom}$, $^3J(HH) = 5.9$ Hz); 2.41, 2.14, 2.07 and 2.01 (4s whose relative importance is 1:4:1:4, 6H, $2CH_3$).

3.1.9. Synthesis of compound ***10a***

To a solution of **2** (0.150 g, 0.165 mmol) in chlorobenzene (20 ml), was added (0.071 g, 0.42 mmol) of ethyl phenylpropyonate. The reaction mixture was heated under reflux for 2 h. The colour changed from orange to dark green. The solvent was evaporated and the resulting solid was dissolved in dichloromethane and filtered through a Celite column (4 cm) to remove any traces of palladium metal. The green-yellow solution was evaporated and **10a** was obtained after washing with pentane as a yellow-green solid (0.53 g, 40%). Anal. Found: C, 79.09; H, 5.39; N, 3.48. $C_{26}H_{21}NO_2 + 1/4\ CH_2Cl_2$ calcd.: C, 78.75; H, 5.37; N, 3.50%. ^1H NMR ($CDCl_3$): δ 8.38–7.31 (m, $12H_{arom}$); 6.51 (s, $1H_{arom}$); 3.84 (q, 2H, OCH_2); 3.03 (s, 3H, NCH_3); 0.30 (t, 3H, CH_3, $^3J(HH) = 7.1$ Hz).

3.1.10. Synthesis of compound ***10b***

To a solution of **2** (0.300 g, 0.331 mmol) in chlorobenzene (15 ml), was added dropwise a solution of dimethylacetylene dicarboxylate (0.094 g, 0.662 mmol) in chlorobenzene (10 ml). The reaction mixture was heated for 2 h at 75–80°C and the solution turned from orange to dark brown. The solvent was evaporated and the resulting solid was eluted through an alumina column (10 cm) using Et_2O/CH_2Cl_2 (2:1) as an eluant. Compound **10b** was obtained as a bright orange solid after removal of the solvent and washing with pentane (0.016 g, 7%). Anal. Found: C, 72.23; H, 4.99; N, 3.55%. $C_{21}H_{17}NO_4$ calcd.: C, 72.61; H, 4.93; N, 4.03. ^1H NMR ($CDCl_3$): δ 8.37–7.39 (m, $7H_{arom}$); 6.57 (s, $1H_{arom}$); 3.98 and 3.85 (2s, 6H, OCH_3); 3.25 (s, 3H, NCH_3).

3.1.11. Synthesis of compound ***11a***

To a solution of **3** (0.862 g, 1 mmol) in chlorobenzene (40 ml), was added diphenylacetylene (0.712 g, 4 mmol). The reaction mixture was heated under reflux for 3 h and the solution turned from orange to dark green. The solvent was evaporated and the resulting solid was passed through an alumina column (10 cm) first eluting with pentane (150 ml) to eliminate the excess of diphenylacetylene. Compound **11a** was eluted with Et_2O (150 ml) and obtained after removal of the solvent as a yellow-green solid (0.345 g, 50%). Anal. Found: C, 89.84; H, 6.06. N, 3.51. $C_{26}H_{21}N$ calcd.: C, 89.87; H, 6.09; N, 4.03%. ^1H NMR ($CDCl_3$): δ 7.26–6.90 (m, $14H_{arom}$); 6.30 (d, $1H_{arom}$, $^3J(HH) = 7.1$ Hz); 6.05 (d, $1H_{arom}$, $^3J(HH) = 6.6$ Hz); 3.46 (q, 2H, NCH_2); 1.11 (t, 3H, $NCCH_3$, $^3J(HH) = 6.9$ Hz).

3.1.12. Synthesis of compound ***11b***

To a solution of **3** (0.431 g, 0.50 mmol) in chlorobenzene (30 ml), was added ethyl phenyl propyonate (0.174 g, 1 mmol). The reaction mixture was heated under reflux for 2 h and the solution turned dark green. The solvent was evaporated and the resulting solid was eluted from an alumina column (8 cm) first eluting with pentane to remove the unreacted acetylene. Compound **11b** was eluted with Et_2O (100 ml) and obtained after removing the solvent as an orange solid (0.168 g, 50%). Anal. Found: C, 80.20; H, 6.01; N, 3.89. $C_{23}H_{21}NO_2$ calcd.: C, 80.47; H, 6.12; N, 4.09%. ^1H NMR ($CDCl_3$): δ 7.45–6.31 (m, $10H_{arom}$); 3.82 (q, 2H, OCH_2); 3.43 (q, 2H, NCH_2); 1.09 (t, 3H, $NCCH_3$, $^3J(HH) = 6.9$ Hz); 0.81 (t, 3H, $OCCH_3$, $^3J(HH) = 7.1$ Hz).

TABLE 1. X-Ray experimental data of compound **9**

Formula	$C_{24}H_{21}ClN_2Pd, CH_2Cl_2$
Molecular weight	564.2
Colour	Yellow
Crystal system	Monoclinic
a (Å)	12.921(3)
b (Å)	11.747(3)
c (Å)	16.413(4)
β (°)	100.93(2)
Volume (Å^3)	2446.0
Z	4
D_{calc} (g cm^{-3})	1.532
Wavelength (Å)	0.7093
μ (cm^{-1})	10.936
Space group	$P2_1/c$
Diffractometer	Enraf-Nonius CAD4-F
Crystal dimensions (mm^3)	0.22×0.24×0.32
Temperature (°C)	20
Radiation	Mo Kα graphite monochromated
Mode	θ–2θ
Scanspeed	Variable
Scan width (°)	$1.00 + 0.34 \times \mathrm{tg}(\theta)$
Octants	$\pm h + k + l$
$\theta_{min/max}$ (°)	2/24
Number of data collected	4676
Number of data with $I > 3\sigma(I)$	3224
$Abs_{min/max}$	0.90/1.14
$R(F)$	0.028
$R_w(F)$	0.045
p	0.08
GOF	1.001

TABLE 2. Selected bond distances (Å) and angles (°) of compound **9**

Pd–Cl1	2.311(1)	Cl1–Pd–N2	89.5(1)
Pd–N1	2.028(3)	Cl1–Pd–C1	94.9(1)
Pd–N2	2.143(3)	N1–Pd–N2	95.4(1)
Pd–C1	1.970(3)	N1–Pd–C1	80.1(1)
N1–C7	1.300(4)	Cl1–Pd–N1	174.9(1)
N1–C9	1.434(5)	C7–N1–C9	121.7(3)
C6–C7	1.464(5)	N1–C7–C6	114.2(3)

3.2. X-Ray data collection and structure determination of compound 9

Suitable crystals of **9** were obtained by slow evaporation of a CH_2Cl_2/hexane solution at room temperature as a 1:1 CH_2Cl_2 solvate. All experimental data are given in Table 1. The resulting data sets were transferred to a VAX computer, and for all subsequent calculations the Enraf–Nonius Molen package was used [18]. All the crystallographic data were obtained on an Enraf-Nonius CAD4-F diffractometer with graphite-monochromated molybdenum radiation (λ Mo Kα = 0.70930 Å) at an ambient temperature of 20 ± 2°C. Three standard reflections were measured every 1 h during the entire data collection period. No significant changes in intensity were observed. The data were converted to intensities and corrected for Lorentz and polarization factors. Semiempirical absorption corrections were applied from ϕ scans of four reflections. The structure was solved using the heavy atom technique. The hydrogen atoms were introduced in calculations in computed positions (C–H = 0.95 Å) with isotropic temperature factors such as $B(H) = 1.3B_{eq}(C)$ Å^2 but were not refined. Full least-squares refinements were done using $\sigma^2(F^2) = \sigma^2_{counts} + (pI)^2$. A final difference map revealed no significant maxima. The scattering factor coefficients and anomalous dispersion coefficients are from ref. 19.

TABLE 3. Table of positional parameters and corresponding e.s.d.s

Atom	x	y	z	B (Å^2) [a]
Pd	0.19977(2)	0.03586(2)	0.07808(1)	3.223(5)
Cl1	0.19511(8)	0.06283(8)	0.21679(5)	4.67(2)
N1	0.2044(2)	0.0275(2)	−0.0446(2)	3.64(6)
N2	0.1527(2)	−0.1377(2)	0.0884(2)	3.75(6)
C1	0.2399(2)	0.1940(3)	0.0588(2)	3.57(6)
C2	0.2621(3)	0.2829(3)	0.1167(3)	4.77(8)
C3	0.2861(3)	0.3899(3)	0.0920(3)	5.6(1)
C4	0.2887(3)	0.4128(4)	0.0092(3)	6.0(1)
C5	0.2692(3)	0.3276(3)	−0.0488(3)	4.95(8)
C6	0.2463(2)	0.2187(3)	−0.0232(2)	3.71(7)
C7	0.2251(3)	0.1217(3)	−0.0799(2)	4.00(7)
C8	0.2294(4)	0.1303(4)	−0.1698(2)	5.9(1)
C9	0.1848(3)	−0.0768(3)	−0.0903(2)	3.88(7)
C10	0.0874(3)	−0.1004(4)	−0.1342(2)	4.99(9)
C11	0.0659(3)	−0.2070(4)	−0.1735(3)	5.8(1)
C12	0.1441(3)	−0.2856(4)	−0.1689(3)	5.69(9)
C13	0.2465(3)	−0.2628(3)	−0.1257(2)	4.53(8)
C14	0.2691(3)	−0.1576(3)	−0.0829(2)	3.96(7)
C15	0.3698(3)	−0.1357(3)	−0.0368(2)	4.71(8)
C16	0.4483(3)	−0.2166(4)	−0.0344(3)	6.3(1)
C17	0.4262(4)	−0.3190(4)	−0.0789(3)	6.7(1)
C18	0.3297(3)	−0.3422(4)	−0.1220(3)	6.0(1)
C19	0.0576(3)	−0.1739(3)	0.0528(2)	4.58(8)
C20	0.0204(3)	−0.2820(3)	0.0616(3)	4.99(9)
C21	0.0829(3)	−0.3593(3)	0.1123(2)	4.58(8)
C22	0.1833(3)	−0.3216(3)	0.1488(3)	5.08(9)
C23	0.2143(3)	−0.2133(3)	0.1359(2)	4.47(8)
C24	0.0433(4)	−0.4750(4)	0.1287(4)	6.6(1)
C25	0.5257(5)	0.6014(5)	0.2760(4)	8.3(1)
CL2	0.5000(2)	0.4595(2)	0.2950(1)	10.79(5)
CL3	0.4899(1)	0.6364(2)	0.1703(1)	10.02(5)

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

4. Supplementary material available

Tables of full lists of distances and angles, positional parameters of hydrogen atoms, general displacement parameters expressions (U), and observed and calculated structure factors for compound **9** (20 pages) can be obtained from the authors.

Acknowledgements

We thank the Hariri Foundation (Lebanon) for a Fellowship (to N.S.B.), the Commission of the European Communities for financial support (Contract no. SC1-0319-C (GDF)) and Mrs. A. Degremont for technical assistance.

References

1 (a) M. Pfeffer, *Recl. Trav. Chim. Pays-Bas, 109* (1990) 567 and refs. therein; (b) G. Wu, J. Geib, A.L. Rheingold and R.F. Heck, *J. Org. Chem., 53* (1988) 3238.
2 N. Beydoun and M. Pfeffer, *Synthesis, 8* (1990) 729.
3 J. Dehand, C. Mutet and M. Pfeffer, *J. Organomet. Chem., 209* (1981) 255.
4 G. van Koten, J.T.B.H. Jastrzebski, J.G. Noltes, W.M.G.F. Pontenagel, J. Kroon and A.L. Spek, *J. Am. Chem., Soc., 100* (1978) 5021.
5 P.W. Clark and S.F. Dyke, *J. Organomet. Chem., 259* (1983) C17.
6 B.N. Cockburn, D.V. Howe, T. Keating, B.F.G. Johnson and J. Lewis, *J. Chem. Soc., Dalton Trans.*, (1973) 404.
7 A. Avshu, R.D. O'Sullivan, A.W. Parkins, N.W. Alcock and R.M. Countryman, *J. Chem. Soc., Dalton Trans.*, (1983) 1619.
8 J. Dehand, J. Jordanov and M. Pfeffer, *J. Chem. Soc., Dalton Trans.*, (1976) 1553.
9 M. Postel, M. Pfeffer and J.G. Riess, *J. Am. Chem. Soc., 99* (1977) 5623.
10 F. Maassarani, M. Pfeffer, G. Le Borgne and D. Grandjean, *Organometallics, 5* (1986) 1511; F. Maassarani, M. Pfeffer and G. Le Borgne, *Organometallics, 6* (1987) 2043.

11 K. Hiraki, Y. Fuchita and K. Takechi, *Inorg. Chem., 20* (1983) 4316 and refs. therein.
12 C. Arlen, M. Pfeffer, O. Bars and D. Grandjean, *J. Chem. Soc., Dalton Trans.*, (1986) 359.
13 J. Dupont, N. Beydoun and M. Pfeffer, *J. Chem. Soc., Dalton Trans.*, (1989) 1715.
14 See for example: R. Gottlieb and J.L. Neumeyer, *J. Am. Chem. Soc., 98* (1976) 7108.
15 J. March, *Advanced Organic Chemistry, Reactions, Mechanisms and Structure*, 3rd edition, Wiley, New York, 1985.
16 D.G. Thomas, J.H. Billman and C.E. Davis, *J. Am. Chem. Soc., 68* (1946) 895.
17 R. Scholl, C. Seer and R. Weitzenböck, *Chem. Ber., 43* (1910) 2202.
18 B.A. Frenz, The Enraf-Nonius CAD4-SDP, in R. Olthof-Hazekamp, H. van Koningsveld and G.C. Bassi (eds.), *Computing in Crystallography*, University Press, Delft, 1978, pp. 64–71.
19 D.T. Cromer and J.T. Waber, *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, Vol. IV.