CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200800510

Metal-Free and Pd^{II}-Promoted [2+3] Cycloadditions of a Cyclic Nitrone to Phthalonitriles: Syntheses of Oxadiazolines as well as Phthalamide–Pd^{II} and Dihydropyrrolyl-iminoisoindolinone–Pd^{II} Complexes with High Catalytic Activity in Suzuki–Miyaura Cross-Coupling Reactions

Jamal Lasri,[a] Maximilian N. Kopylovich,[a] M. Fátima C. Guedes da Silva,[a, b] M. Adília Januário Charmier,[a, b] and Armando J. L. Pombeiro*[a]

Abstract: The previously unknown reactions between phthalonitriles, 1,2-$(CN)_2(C_6)R^1R^2R^3R^4$ **1** (**1a**, $R^1=R^2=R^3=R^4=H$; **1b**, $R^1=R^2=R^4=H$, $R^3=CH_3$; **1c**, $R^1=R^4=H$, $R^2=R^3=Cl$; **1d**, $R^1=R^2=R^3=R^4=Cl$; **1e**, $R^1=R^2=R^3=R^4=F$), and a cyclic nitrone, $^{-}O^{+}N{=}CHCH_2CH_2CMe_2$ **2**, proceed under heating in a sealed tube to give phthalimides **3**, 2-oxadiazolyl-benzonitriles **4** or *ortho*-bis(oxadiazolyl)tetrafluorobenzene **4e′**. In the presence of palladium(II) chloride, phthalonitriles **1** react with **2** at room temperature, to give bis(pyrrolidin-2-ylidene)phthalamide Pd^{II} complexes **5** via metal-promoted rupture of the N–O bond of the oxadiazoline ring. The ketoimine ligands thus generated can be liberated from the metal by displacement with a diphosphine. Although the first [2+3] cycloaddition of **2** to **1** can occur in the absence of the metal to give the monocycloadducts **4**, the second [2+3] coupling at the still-unreacted cyano group requires its activation by coordination to Pd^{II}, affording complexes **6** containing two ligated oxadiazolyl-benzonitriles. These ligands undergo either i) further cycloaddition with **2** to afford ultimately (upon rearrangement) the bis(pyrrolidinylidene)phthalamide complexes **5** or ii) N–O bond cleavage in the oxadiazoline ring with *intramolecular* attack of the imine nitrogen on the cyano carbon and bridging to a second Pd^{II} center to afford dimeric palladium(II) complexes **7**, with chloride bridges, that bear a dihydropyrrolyl-iminoisoindolinone, a new type of ligand.

The compounds were characterized by IR, ^1H, and ^{13}C NMR spectroscopy, ESI MS or FAB^+ MS, elemental analyses and, in the case of **4c**, **5a**, **5c**, and **7c**, also by X-ray diffraction analysis. Complexes **5a** and **7c** show high catalytic activity for the Suzuki–Miyaura cross-coupling reaction of bromobenzene and phenylboronic acid and give biphenyl in high yields with turnover frequencies (TOFs) of up to $9.0\times10^5\ h^{-1}$.

Keywords: heterocycles · iminoisoindolinones · palladium · phthalonitriles · Suzuki–Miyaura reaction

Introduction

Heterocycles have long been a research area of great interest, owing in part to their catalytic[1] and biomedical[2] applications. They are of widespread occurrence in nature, for example, in alkaloids. In this area, although derivatives of the lactam or oxadiazoline rings have applications as antitumor agents or as antibiotics,[3] those containing indole or isoindole ring systems are important intermediates in the synthesis of phthalocyanins.[4,5] Aromatic heterocyclic compounds also find applications based on their photochemical properties or as luminescent molecular sensors, and in supramolecular (polynuclear) complexes with interesting optical or magnetic properties.[6] On the other hand, because pallad-

[a] Dr. J. Lasri, Dr. M. N. Kopylovich, Dr. M. F. C. Guedes da Silva, Dr. M. A. J. Charmier, Prof. Dr. A. J. L. Pombeiro
Centro de Química Estrutural, Complexo I
Instituto Superior Técnico, TU Lisbon
Av. Rovisco Pais, 1049–001 Lisbon (Portugal)
Fax: (+351) 218-464-455
E-mail: pombeiro@ist.utl.pt

[b] Dr. M. F. C. Guedes da Silva, Dr. M. A. J. Charmier
Universidade Lusófona de Humanidades e Tecnologias
ULHT Lisbon, Av. Campo Grande no 376
1749–024, Lisbon (Portugal)

ium(II) complexes have found many relevant applications in synthetically useful catalytic reactions,[7] the combination of palladium with heterocyclic ligands is expected to lead to new active species.

The main general aims of the current work are:

1) To find new types of synthetic reactions for heterocyclic compounds.
2) To synthesize novel heterocycles.
3) To study the influence of palladium(II) in such reactions.
4) To prepare novel types of palladium(II) complexes with heterocyclic ligands.
5) To find a catalytic application of such Pd^{II} complexes in a recognized important synthetic reaction.

With aims 1–4 in mind, we have selected 1,3-dipolar cycloaddition reactions, which constitute a powerful tool to create C–N and C–O bonds, for the synthesis of a great variety of heterocycles.[8] However, one of the main problems of cycloadditions is that various dipolarophiles, such as organonitriles, do not commonly undergo 1,3-dipolar cycloadditions due to their low reactivity.[9] Second, a heterocycle synthesis often consists of sequential reactions that can involve one or more thermodynamically unfavourable steps. To overcome such difficulties, alternative metal-mediated cycloadditions have been the object of extensive current investigations due to the possible key role of a metal for their promotion.[9]

As a continuation of our project on 1,3-dipolar cycloaddition reactions of free and metal-activated organonitriles with various dipoles, for example, nitrones,[10–12] we have now extended the work, for the first time, to phthalonitriles (substituted 1,2-dicyanobenzenes). Our objective (within the above aims 1–4) is to study the previously unknown [2+3] cycloaddition reactions of cyclic and acyclic nitrones with these aromatic dinitriles in pure organic chemistry, to synthesize novel N-heterocycles, and to investigate the effect of a coordinating Pd^{II} center on such reactions.

One or both of the cyano groups of a phthalonitrile can react, in the latter case in similar or different ways, allowing the formation of a variety of products, namely phthalimides and fused mono- and bis-oxadiazolines, attached to the phenyl ring of the phthalonitrile precursor, depending on electronic effects of the substituents at this ring.

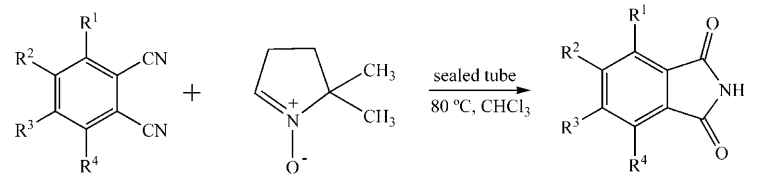
Unpredictable results were obtained when the reactions were undertaken in the presence of palladium(II) chloride (aim 3) giving rise to unexpected substituted bis(pyrrolidin-2-ylidene)phthalamide-Pd^{II} complexes (aim 4) which, by subsequent ligand replacement, allowed the liberation of the corresponding novel free phthalamides, for example, N^1,N^2-bis(5,5-dimethylpyrrolidin-2-ylidene)-3,4,5,6-tetrafluorophthalamide (aim 2), structurally related with an important class of heterocyclic compounds with promising biological activity.[13] Finally, by this process, we synthesized a novel type of dimeric palladium complex (aim 4) with the 2-dihydropyrrolyl-iminoisoindolinone ligand, which, to our knowledge, is the first example of such a type of compound reported to date.

Concerning aim 5 (the search for a catalytic application), we have focused our attention on the Suzuki–Miyaura reaction,[14] one of the most powerful C–C cross-coupling reactions, which is known to be catalyzed by some Pd^{II} complexes, which contain N ligands. We have thus found that representatives of our mono- and dinuclear complexes act as very active catalysts for the cross-coupling reaction of bromobenzene and phenylboronic acid to give biphenyl in high yield with a turnover frequency (TOF) reaching $9.0\times10^5\ h^{-1}$.

Results and Discussion

Organic reactions: Because, to our knowledge, the reactivity of nitrones toward phthalonitriles has not yet been reported, in spite of its potential synthetic value, we decided to study the reactions of the cyclic nitrone $^{-}O^{+}N{=}CHCH_2CH_2CMe_2$ **2** with various phthalonitriles $1,2\text{-}(CN)_2(C_6)R^1R^2R^3R^4$ **1**, by heating their $CHCl_3$ solutions in a sealed tube at 80 °C. The resulting products, isolated by column chromatography on silica (CH_2Cl_2 as eluent), depend on the nature of the substituents in the starting phthalonitriles **1**. Hence, the reactions of **1a** ($R^1=R^2=R^3=R^4=H$) and its methyl derivative **1b** ($R^1=R^2=R^4=H$, $R^3=CH_3$) with the cyclic nitrone **2**, under the above conditions, give the phthalimide **3a** and the 5-methyl derivative **3b**, respectively, in moderate yields (ca. 50%) (Scheme 1). No reaction was observed at room temperature or under refluxing $CHCl_3$ at ambient pressure.

The formation of **3** can be proposed (Scheme 2) to occur by hydrolysis of the nitrone (a known reaction[15]) to give the corresponding α-hydroxy hydroxylamine (i.e. 5,5-dimethylpyrrolidine-1,2-diol) **I** which would react with the phthalonitrile in a comparable way to that reported[16] for the hydroxylamine Et_2NOH, that is, by nucleophilic addition to a CN group with CN–CN coupling to give an imino species **II**. Further transformation with liberation of 5,5-dimethyl-3,4-dihydropyrrol-2-ol **III** would form the 3-iminoisoindolin-1-one **IV**, which, upon hydrolysis, would furnish[17] the phthalimide product **3**.

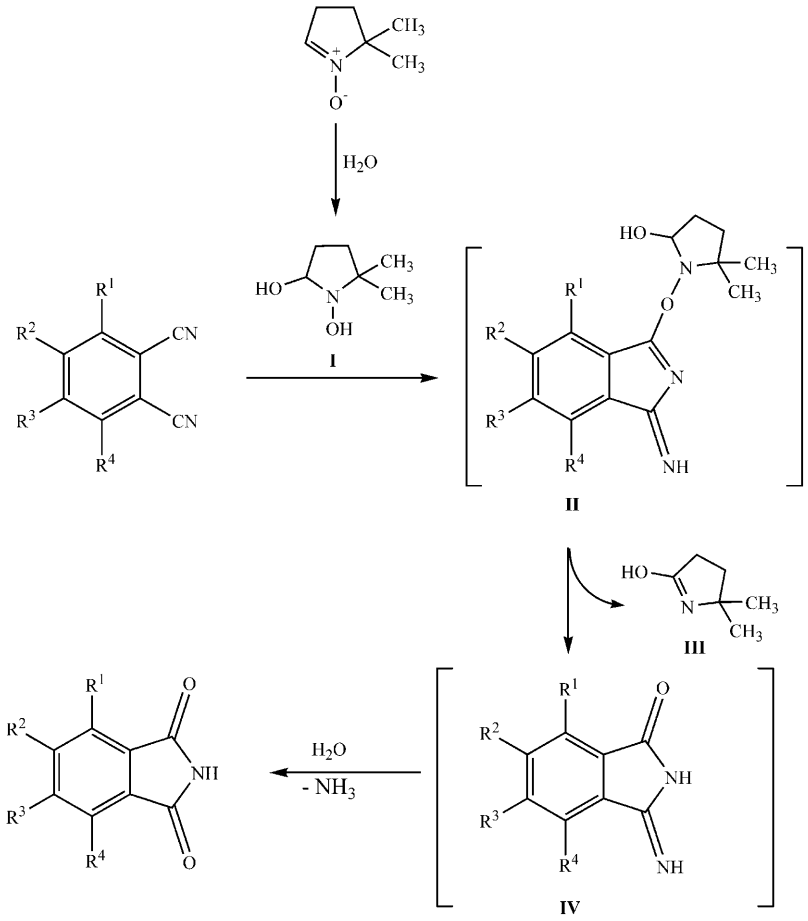


1a: $R^1=R^2=R^3=R^4=H$
1b: $R^1=R^2=R^4=H$, $R^3=CH_3$

2

3a: $R^1=R^2=R^3=R^4=H$
3b: $R^1=R^2=R^4=H$, $R^3=CH_3$

Scheme 1. Synthesis of phthalimides from phthalonitriles and cyclic nitrone.

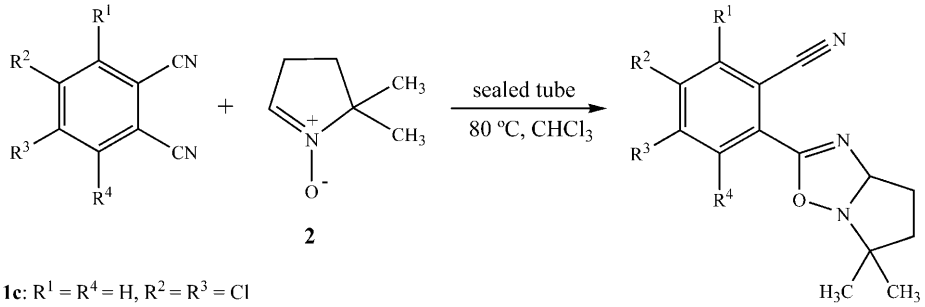


Scheme 2. Proposed mechanism of phthalimide synthesis.

In contrast, the reactions of the phthalonitriles **1c–e** containing an electron-withdrawing group (**1c**, $R^1=R^4=H$, $R^2=R^3=Cl$; **1d**, $R^1=R^2=R^3=R^4=Cl$; **1e**, $R^1=R^2=R^3=R^4=F$) with one or two equivalents of cyclic nitrone **2**, under the above experimental conditions (sealed tube, 80 °C, $CHCl_3$) afford, in moderate to good yields (70–35 %), the 2-(oxadiazolyl)-benzonitrile derivatives **4c–4e**, derived from a single-pot [2+3] cycloaddition reaction of the nitrone **2** to the phthalonitriles **1c–1e** (Scheme 3), a known[18] type of nitrile and nitrone coupling. It is worth mentioning that the attempts to obtain similar products by using the acyclic nitrone $(4\text{-}MeC_6H_4)CH{=}(Me)N^+O^-$, instead of the more reactive cyclic one, failed and led to the formation of oily mixtures of unidentified products.

When the reactions of the phthalonitriles **1c** and **1d** were undertaken with two equivalents of the nitrone **2** and under more drastic conditions (prolonged heating and/or higher concentrations of the reagents in the $CHCl_3$ solution) than those normally used, the formation of mixtures with compounds (5–2 % yields) derived from [2+3] cycloadditions to both nitriles was detected by ^1H and ^{13}C NMR spectroscopy and FAB MS.

The phthalimides **3** and the 2-(oxadiazolyl)-benzonitrile products **4c–e** were characterized by IR, ^1H and ^{13}C NMR spectroscopy, FAB^+ MS, elemental analyses and, for **4c**, by single-crystal X-ray diffraction. In the IR spectra of compounds **4**, ν(N≡C) appears in the same range of wavenumbers (2234–2242 cm^{-1}) as that observed for the starting phthalonitriles **1c–1e**, whereas the detection of new bands at 1628–1680 cm^{-1} assigned to ν(N=C) confirms the formation of the oxadiazoline; additionally, the detection of ν(NC=O) vibrations at 1735–1742 cm^{-1} can be accounted for by the appropriate tautomeric resonance forms of the oxadiazoline ring. The ^1H and ^{13}C NMR spectra of **4** confirm that the compounds contain both an oxadiazoline and a nitrile moiety. In the former spectrum, the N–C*H*–N resonances are detected at $\delta=5.75$–5.85 ppm, and, in the latter spectrum, the N–*C*H–N resonances appear at $\delta=91.7$–92.5 ppm, whereas the N≡*C* signals are observed in the $\delta=109.3$–



1c: $R^1=R^4=H$, $R^2=R^3=Cl$
1d: $R^1=R^2=R^3=R^4=Cl$
1e: $R^1=R^2=R^3=R^4=F$

4c: $R^1=R^4=H$, $R^2=R^3=Cl$
4d: $R^1=R^2=R^3=R^4=Cl$
4e: $R^1=R^2=R^3=R^4=F$

Scheme 3. Synthesis of 2-(oxadiazolyl)benzonitrile derivatives **4c–4e**.

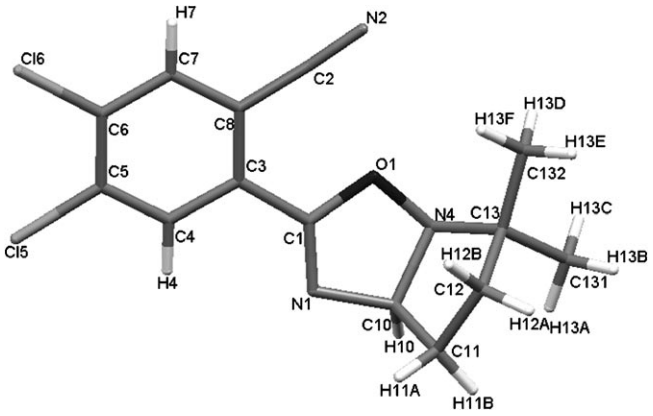


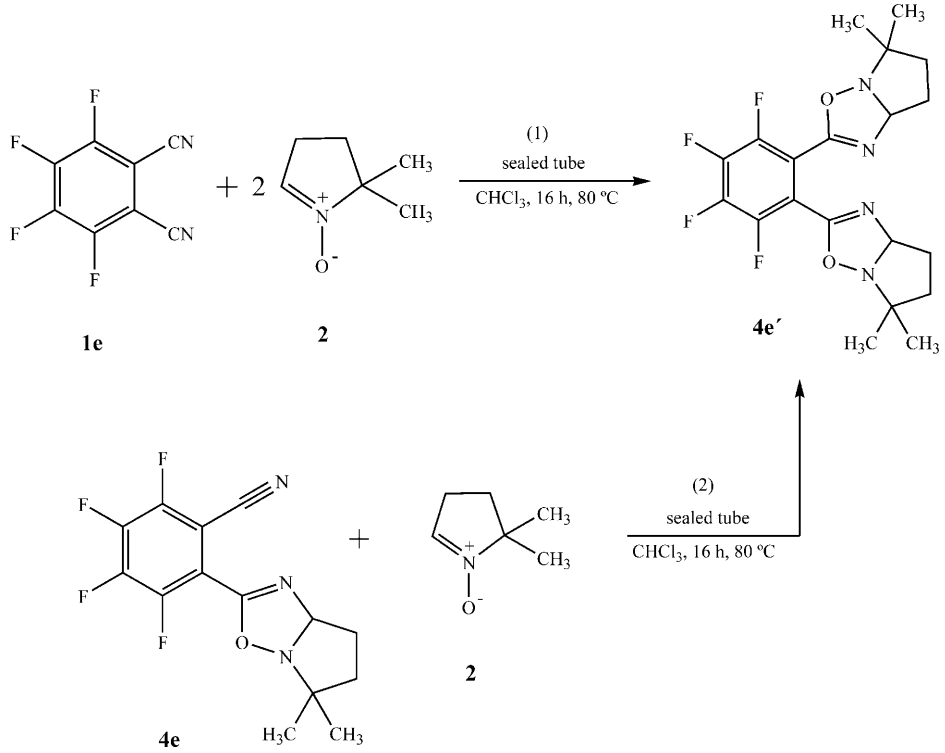
Figure 1. Molecular structure of 4,5-dichloro-2-(5,5-dimethyl-5,6,7,7*a*-tetrahydroazolo[1,2-*b*,1,2,4]oxadiazol-2-yl)benzonitrile **4c** with atomic numbering scheme. Selected bond lengths [Å] and angles [°]: Cl5–C5 1.729(3), O1–N4 1.493(3), O1–C1 1.358(3), N1–C1 1.260(4), N1–C10 1.472(3), N2–C2 1.147(5), N4–C10 1.511(4), N4–C13 1.504(4), C1–C3 1.482(4), C2–C8 1.449(4), C3–C4 1.382(4), C10–C11 1.542(4); N4-O1-C1 105.05(18), C1-N1-C10 106.2(2), O1-N4-C10 101.83(17), N4-C13-C132 111.7(2), O1-N4-C13 106.88(19), O1-C1-N1 118.6(2), O1-C1-C3 115.6(2), N1-C1-C3 125.8(2), N2-C2-C8 173.6(3), N1-C10-C11 111.5(2).

116.1 ppm range. The single-crystal X-ray diffraction analysis of **4c** (Figure 1) also confirms the formulation. The cyano C2≡N2 triple bond length, 1.147(5) Å, and the imine double bond C1=N1 length, 1.260(4) Å, are in accord with the reported[19] average values of 1.144 and 1.279 Å, respectively. It can also be seen that the N1=C1–O1 double bond is delocalized, which is in accord with the above IR data (bands at ca. 1740 cm^{-1}).

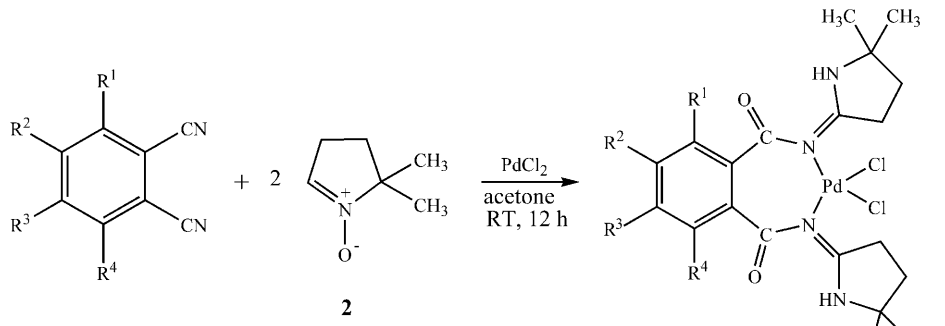
Curiously, the reaction of tetrafluorophthalonitrile **1e** with two equivalents of the nitrone **2** in a sealed tube ($CHCl_3$, 80 °C) for an extended period (16 h instead of 3 h for the formation of the monooxadiazoline **4e**) proceeds further to give the bisoxadiazoline **4e′**, in moderated yield (30 %) (Scheme 4, reaction 1). This product is also obtained (Scheme 4, reaction 2) by treatment of the mono-cycloadduct **4e** with one equivalent of the nitrone **2** ($CHCl_3$, 16 h, 80 °C). The formation of **4e′** from the reaction of **1e** with **2** is thus believed to proceed via the mono-cycloadduct **4e** in which the cyano group, activated by the four fluoro substituents of the phenyl ring, undergoes, after a prolonged reaction time, a further [2+3] cycloaddition with the cyclic nitrone **2**, converting into the symmetrical *ortho*-bis(oxadiazolyl)tetrafluorobenzene **4e′**. The IR spectrum of **4e′** does not exhibit any band that could be assigned to ν(N≡C) and the NMR data also prove that the compound was isolated without ring-opening by N–O bond rupture of the oxadiazoline ring, in contrast to what we have recently observed[12] in other cases.

Inorganic template synthesis: In this second part of the work, we investigated the reactions of the phthalonitriles with the cyclic nitrone in the presence of palladium chloride ($PdCl_2$), thus comparing the reactivity with that in the absence of this metal site and investigating the Pd^{II}-activating (and templating) effect.

Treatment of the phthalonitriles **1** with two equivalents of the cyclic nitrone **2** and one equivalent of $PdCl_2$ in acetone at room temperature for 12 h gave the corresponding bis(-pyrrolidin-2-ylidene)phthalamide Pd^{II} complexes **5** in good yields (73–90 %) (Scheme 5). Elemental analyses, FAB^+ MS, IR, ^1H, and ^{13}C NMR spectra, and X-ray data (for **5a** and **5c**) confirm the proposed formulas. For example, comparison of the IR spectra of these complexes with those of the starting phthalonitriles shows that the C≡N stretching vibrations are replaced by the strong ν(NC=O) and ν(C=N) vibrations at approximately 1731 and 1633 cm^{-1}, respectively and that the ν(NH) band at 3237–3433 cm^{-1} emerges. Moreover, the ^{13}C NMR resonances at $\delta \approx 169.0$ and 173.9 ppm are assigned to the N=*C*NH and N*C*=O moieties, respectively. In the ^1H NMR spectra, the N*H* resonances are detected at $\delta \approx 10.7$ ppm and confirm the N–O ring cleavage.



Scheme 4. Synthesis of bisoxadiazoline **4e′** from 1) phlathonitrile **1e** and 2) from oxadiazoline **4e**.



2

1a: $R^1 = R^2 = R^3 = R^4 = H$
1b: $R^1 = R^2 = R^4 = H$, $R^3 = CH_3$
1c: $R^1 = R^4 = H$, $R^2 = R^3 = Cl$
1d: $R^1 = R^2 = R^3 = R^4 = Cl$
1e: $R^1 = R^2 = R^3 = R^4 = F$

5a: $R^1 = R^2 = R^3 = R^4 = H$
5b: $R^1 = R^2 = R^4 = H$, $R^3 = CH_3$
5c: $R^1 = R^4 = H$, $R^2 = R^3 = Cl$
5d: $R^1 = R^2 = R^3 = R^4 = Cl$
5e: $R^1 = R^2 = R^3 = R^4 = F$

Scheme 5. Synthesis of palladacycles **5**.

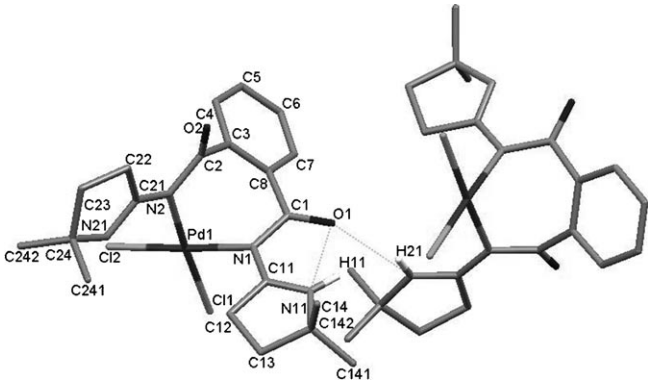


Figure 2. Partial stick representation of the crystal packing diagram of complex **5a** with atomic numbering scheme (hydrogen atoms except of H11 and H21 and solvent molecules are omitted for clarity). Selected bond lengths [Å] and angles [°]: Pd1−Cl1 2.303(2), Pd1−N1 2.047(7), O1−C1 1.227(10), N1−C11 1.340(14), N1−C1 1.395(10), N11−C11 1.320(12), N11−C14 1.488(14), C1−C8 1.493(15), C11−C12 1.500(12); Cl1-Pd1-Cl2 91.87(9), Cl1-Pd1-N1 89.6(2), Cl1-Pd1-N2 174.9(2), C1-C8-C7 117.9(8), N1-Pd1-N2 85.5(3), Pd1-N1-C1 118.5(7), N1-C11-N11 128.1(7), Pd1-N1-C11 120.3(5), N11-C11-C12 109.8(9), C11-N11-C14 114.0(7), O1-C1-N1 123.8(9), N1-C1-C8 115.9(7). Selected hydrogen bonds: N11−H11···O1 2.11, N21−H21··O1 2.23.

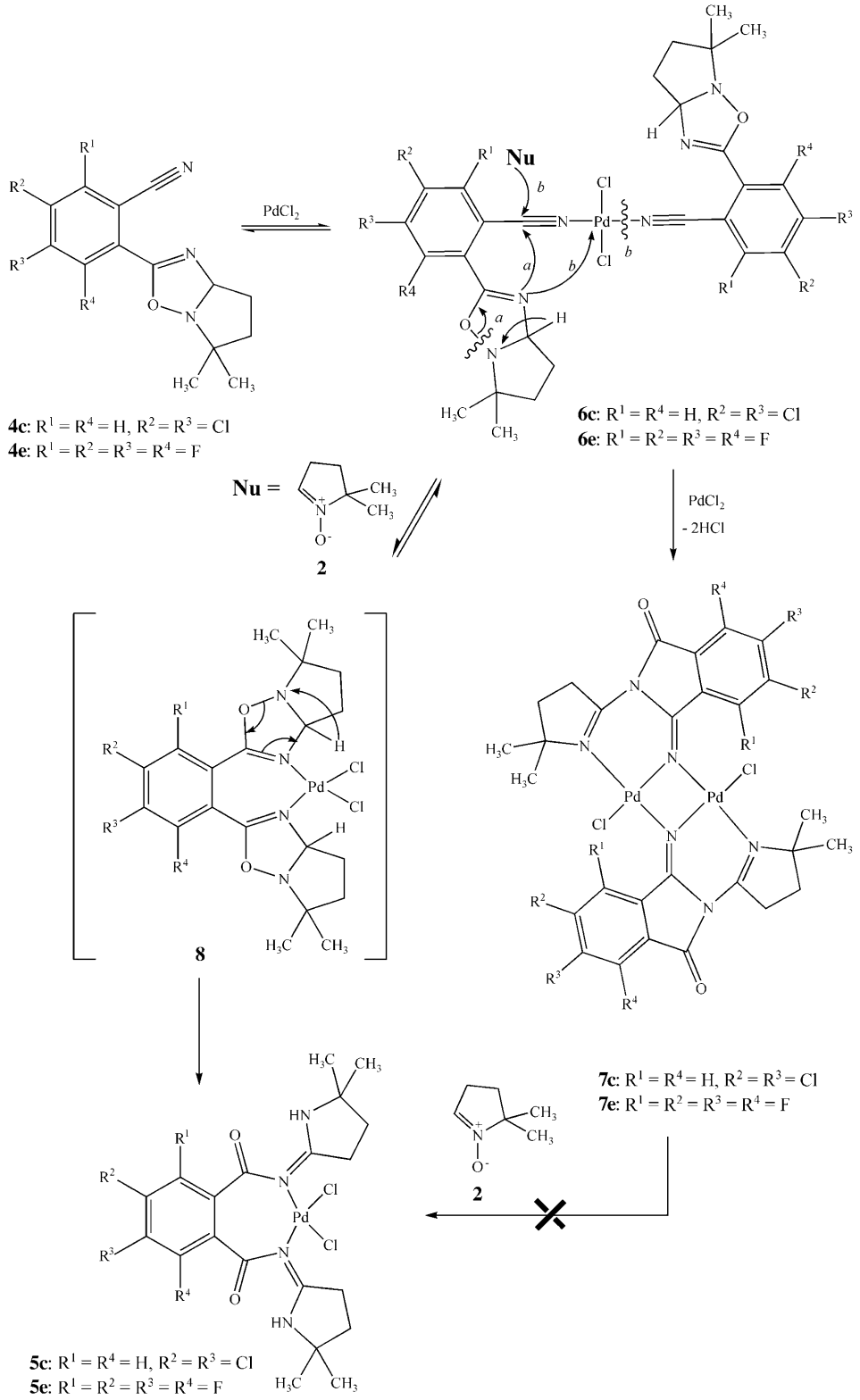
The structures of compounds **5a** (Figure 2) and **5c** were also determined by single-crystal X-ray analysis. These two compounds are quite similar so we will only discuss structure **5a** in more detail. The molecular structure of **5a** shows two strong hydrogen bonds between the amine moieties of the nitrone-derived heterocycle and the keto oxygen O1 atom, one is intramolecular (H11···O1 2.11 Å and N11−H11···O1 121°) and the other one intermolecular (H21···O1 2.2300 Å and N21−H21···O1 144°) (Figure 2b). The C1=O1 and the C2=O2 bond lengths, 1.227(10) and 1.218(10) Å, respectively, within the N−C=O moieties are in accord with the average value, 1.225 Å,[19] for amide derivatives. The similarity of N1−C11, N11−C11, and N1−C1 bond lengths (1.340, 1.320, and 1.395 Å, respectively) shows a significant delocalization of the N1=C11 double bond along the O1-C1-N1-C11-N11 fragment with corresponding formation of the enol form.[12]

However, the reaction of phthalonitriles **1** with the less reactive acyclic nitrone (4-C_6H_4)=CH(Me)N^+O^- in the presence of $PdCl_2$, upon solvent reflux for one day, results in the formation of mixtures of unidentified products.

Mechanistic investigations: Attempted reactions of the phthalonitriles **1** with one equivalent of $PdCl_2$, in the absence of the nitrone, at room temperature or in refluxing acetone for one week resulted in quantitative recovery of the starting materials. Hence, the formation of complexes **5** should not be expected to occur via coordination of the phthalonitrile to Pd.

Surprisingly, treatment of 4,5-dichloro-2-(oxadiazolyl)benzonitrile **4c** or tetrafluoro-2-(oxadiazolyl)benzonitrile **4e** with one equivalent of $PdCl_2$ in acetone for 72 h at room temperature gives the unusual dimers $[\{PdCl(\mu\text{-}N{=}C(R^1R^2R^3R^4C_6)(C{=}O){-}N{-}C{=}N{-}C(CH_3)_2{-}CH_2CH_2)\}_2]$ **7c** ($R^1 = R^4 = H$, $R^2 = R^3 = Cl$) or **7e** ($R^1 = R^2 = R^3 = R^4 = F$), respectively, with the substituted iminoisoindolinone moiety (Scheme 6). Compounds **7c** and **7e** were characterized by conventional methods (see Experimental) and for **7c** (Figure 3) the structure was also authenticated by a single-crystal X-ray diffraction analysis. The IR spectra show the conjugated N−C=N and N−C=O moieties at approximately 1680 and 1750 cm^{-1}, respectively. The ^{13}C NMR spectra exhibit typical C=N and C=O resonances at $\delta \approx 160$ and 164 ppm. The N1=C1, N3=C11, and C2=O1 bonds in **7c** have a significant double-bond character, whereas C1−N2, C11−N2, and C2−N2 are mainly single bonds. Thus, in this case, the π-electron delocalization in the N−C=O and N−C=N moieties is much lower than in compounds **5**. To our knowledge, dimers **7** represent the first examples of metal complexes with 2-dihydropyrrolyl-iminoisoindolinone ligands.

From the mechanistic viewpoint, we believe that dimers **7** are formed via coordination of two molecules of **4** to palladium chloride through the nitrile groups to yield the intermediates **6** (Scheme 6). Subsequent opening of the oxadiazoline ring and spontaneous *intramolecular* attack of the imine nitrogen on the cyano carbon which bridges to a second palladium chloride, with elimination of HCl then occurs (rearrangements partially shown as route *a* on the



Scheme 6. Proposed mechanism for the synthesis of palladacycles **5**.

structural formula of **6**, Scheme 6). We recently discovered similar transformations involving nucleophiles such as oximes and hydroxylamines.[16,20] Although previous reports[21] indicate that, in some cases, *trans*-[$PdCl_2$(organonitrile)$_2$] complexes are not stable in solution, in our work the isolation of the complex **6c** from the reaction mixture was successful and its structure was confirmed by IR and NMR spectroscopy, ESI MS, and elemental analysis (see the Experimental Section). Furthermore, the related intermediate **6e** was detected directly in the reaction mixture by ESI MS. Refluxing acetone solutions of complexes **6** for 48 h leads to the formation of dimers **7**, confirming that compounds **6** are precursors of **7**.

The reactions of the 2-(oxadiazolyl)benzonitriles **4** with one equivalent of the cyclic nitrone **2** and one equivalent of $PdCl_2$ in acetone at room temperature for 12 h give exclusively the corresponding (pyrrolidin-2-ylidene)phthalamide Pd^{II} complexes **5** (Scheme 6). The same products **5** are obtained by treatment of the intermediates **6** with one equivalent of the nitrone **2** in acetone for 12 h at room temperature. In contrast, the dimers **7** do not react with the cyclic nitrone **2** in acetone (room temperature, 72 h).

Attempts to prepare complex **5e** by reaction of the *ortho*-bis(oxadiazolyl)tetrafluorobenzene **4e′** (Scheme 4) with one equivalent of palladium chloride have failed and only the starting materials were recovered quantitatively even after 4 days under solvent reflux, possibly on account of the bulkiness of the oxadiazoline moieties that can hamper their coordination. This provides further support for the formation of complexes **5** via the mono-cycloadducts **4**.

The above results show that the *intermolecular* nucleophilic attack of the cyclic nitrone **2** on the cyano carbon of **6** (Scheme 6, route *b*) to give complexes **5** occurs in preference to the *intramolecular* rearrangement of **6** (via N–O bond cleavage and nucleophilic attack of the imino moiety

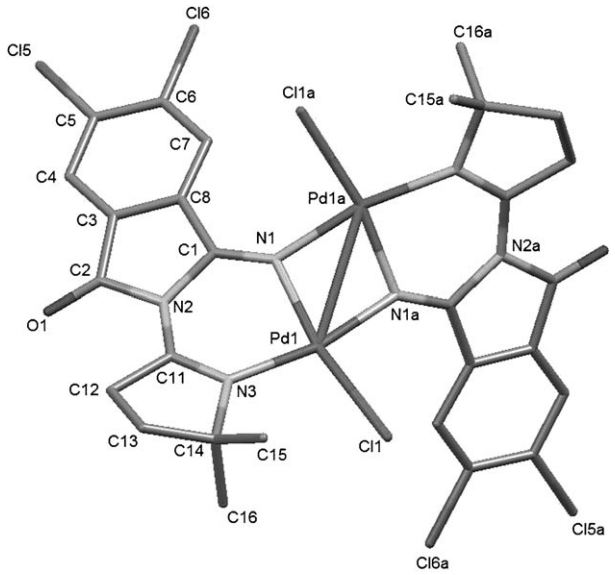


Figure 3. Molecular structure view along the *b* axis of complex **7c** with atomic numbering scheme. Hydrogen atoms and solvent molecules are omitted for clarity. Selected distances [Å] and angles [°]: Pd1–Pd1a 2.9380(8), Pd1–Cl1 2.3266(16), Pd1–N1 1.972(5), Pd1–N3 2.019(4), O1–C2 1.197(8), N1–C1 1.261(7), N2–C2 1.426(7), N2–C11 1.383(7), N2–C1 1.430(8), N3–C1 1.521(8), N3–C11 1.291(7), C1–C8 1.476(8), C2–C3 1.466(8); Cl1-Pd1-N3 100.69(14), Pd1a-Pd1-Cl1 125.64(4), Cl1-Pd1-N1a 91.31(13), N1-Pd1-N3 89.79(18), N1-C1-N2 123.6(5), C1-N2-C11 124.4(5), C1-N2-C2 110.4(5), N2-C11-N3 124.6(5), C11-C12-C13 101.4(5), Pd1-N3-C11 123.2(4), O1-C2-N2 125.7(5). Symmetry transformations used to generate the equivalent atoms: a) $-x, y, 1/2-z$.

to the cyano carbon, route *a*) that would lead to the formation of dimers **7**. In contrast, reactions of **4** with other nucleophiles such as the acyclic nitrone $^{-}O^{+}N(Me)=C(H)-(C_6H_4Me\text{-}4)$, *N,N*-diethylhydroxylamine Et_2NOH or acetone oxime $Me_2C=NOH$ instead of the cyclic nitrone **2**, under the same experimental conditions, afford the dimers **7** as exclusive products. In this case the *intramolecular* rearrangement is more favourable than the *intermolecular* addition, in accord with the lower reactivity of these nucleophiles in comparison with the cyclic nitrone.

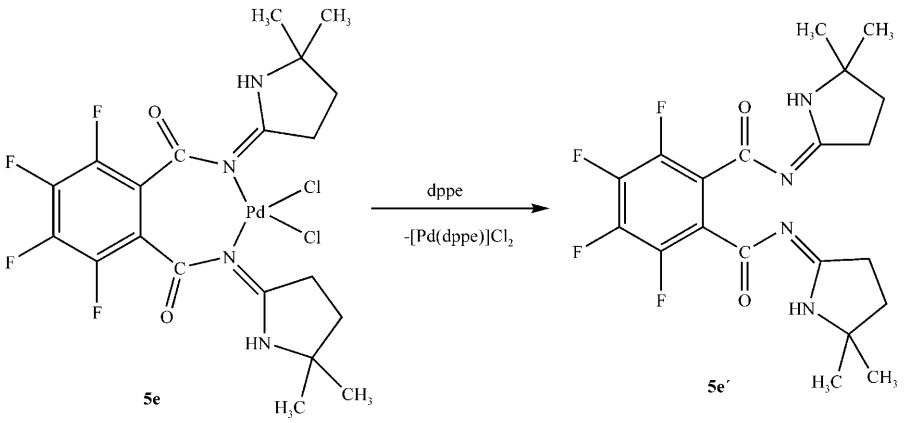
The intermolecular reaction (*b*, Scheme 6) leading to the complexes **5** is believed to proceed via [2+3] cycloaddition of the cyclic nitrone **2** to the cyano moiety of one nitrile ligand in **6** and elimination of the other one to give an unstable bicyclic 1,2,4-oxadiazoline-Pd^{II} intermediate **8** in which the rupture of the N–O bond is promoted by the metal site. The course of this type of reaction, which proceeds through an oxadiazoline–Pt complex related to **8** was demonstrated by us in a previous study.[12] The metal center increases the oxophilic character of the imine N=*C*(R)ON carbon and renders this atom capable of abstracting the oxygen of the O–N group to form the ketoimino moiety N(C=O)=CNH upon rearrangement involving a formal 1,2-*H* shift from the CH carbon of the oxadiazoline ring to the adjacent and deoxygenated N atom.

Liberation of ketoimine 5e′: The possibility of liberation of the ketoimine ligand from a complex **5** is illustrated by displacement with 1,2-bis(diphenylphosphanyl)ethane (dppe) from **5e** (Scheme 7). When precipitation of the colorless compound, $[PdCl_2(dppe)]$ (identified by IR and ^{31}P NMR spectroscopy[22]) was complete, the quantitative formation of the free ketoimine **5e′** was confirmed by IR, ^{1}H, and ^{13}C NMR spectroscopy (see Experimental Section).

Catalysis: Because palladium(II) complexes with two N-coordinated ligands are known[14] to act as catalysts for the Suzuki–Miyaura cross-coupling reaction of bromobenzene (PhBr) and phenylboronic acid ($PhB(OH)_2$) to give biphenyl, we have also tested the possible catalytic applications of representatives of our mono- and dinuclear Pd^{II} complexes of types **5** and **7** in that reaction. We have thus observed that complexes **5a** and **7c** show a very high catalytic activity for the standard Suzuki–Miyaura system (1 equiv of bromobenzene and 1.2 equiv of phenylboronic acid) (Table 1). High isolated yields of biphenyl (up to 97%) are achieved in toluene at 100°C, with K_2CO_3 as a base, with turnover numbers (TON) up to 9.3×10^5 and 9.5×10^5 moles of biphenyl per mole of catalyst, and turnover frequencies (TOF) of up to 1.8×10^5 and 9.0×10^5 moles of biphenyl per mole of catalyst per hour, for **5a** and **7c**, respectively. These results are amongst the best ones so far reported in the field.[23]

Conclusion

The results of this work show that the purely organic reactions between the phthalonitriles **1** and the cyclic nitrone **2** proceed under harsh conditions (heating in a sealed tube) to give phthalimide **3**, 2-(oxadiazolyl)benzonitrile **4**, or *ortho*-



Scheme 7. Liberation of ketoimine **5e′**.

Table 1. Catalytic activity of complexes **5a** and **7c** for the Suzuki–Miyaura cross-coupling reaction of bromobenzene and phenylboronic acid.[a]

Entry	Catalyst [mmol]	t [h]	Yield [%][b]	TON[c]	TOF [h^{-1}][d]
1	**5a** (5×10^{-4})	24	97	9.7×10^{3}	4.1×10^{2}
2	**5a** (5×10^{-4})	1	95	9.5×10^{3}	9.5×10^{3}
3	**5a** (5×10^{-5})	24	94	9.4×10^{4}	3.9×10^{3}
4	**5a** (5×10^{-5})	1	92	9.2×10^{4}	9.2×10^{4}
5	**5a** (5×10^{-5})	0.5	90	9.0×10^{4}	1.8×10^{5}
6	**5a** (5×10^{-6})	24	93	9.3×10^{5}	3.9×10^{4}
7	**5a** (5×10^{-6})	7	90	9.0×10^{5}	1.3×10^{5}
8	**7c** (5×10^{-4})	24	97	9.7×10^{3}	4.1×10^{2}
9	**7c** (5×10^{-5})	24	94	9.4×10^{4}	3.9×10^{3}
10	**7c** (5×10^{-6})	3	95	9.5×10^{5}	3.2×10^{5}
11	**7c** (5×10^{-6})	1	90	9.0×10^{5}	9.0×10^{5}

[a] PhBr (5.0 mmol) + $PhB(OH)_2$ (6.0 mmol) + K_2CO_3 (10.0 mmol) + catalyst + toluene (50 mL), in air, at 100 °C (see Experimental). [b] Moles of biphenyl per 100 moles of PhBr. [c] Turnover number (moles of biphenyl per mole of catalyst). [d] Turnover frequency (moles of biphenyl per mole of catalyst per hour).

bis(oxadiazolyl)tetrafluorobenzene **4e′** derivatives, depending on the nature of substituents in the starting phthalonitriles (an electron-withdrawing substituent, such as F, promotes the [2+3] cycloaddition which can even occur at both cyano groups in tetrafluorophthalonitrile) and on the reaction time. In contrast, the reactions in the presence of a palladium(II) site proceed, under mild conditions, in a controlled way, providing an easy and selective access to bis(pyrrolidin-2-ylidene)phthalamide Pd^{II} complexes **5** via an unprecedented single-pot reaction, in which the spontaneous rupture of the N–O bond of the oxadiazoline ring is promoted by the metal center. The ketoimine ligands thus generated can be successfully liberated from the metal by displacement with dppe.

A first [2+3] cycloaddition of a phthalonitrile **1** with the nitrone **2** can occur in the absence of the metal to give a mono-cycloadduct (2-(oxadiazolyl)benzonitrile **4**), but the second [2+3] coupling at the still-unreacted cyano group requires its activation by coordination to Pd^{II}, to afford a complex **6** with two ligated oxadiazolyl-benzonitriles. These ligands show quite a versatile reactivity and can undergo either i) further cycloaddition with the cyclic nitrone to afford ultimately (upon rearrangement) the (pyrrolidinylidene)phthalamide complexes **5** or ii) N–O bond cleavage in the oxadiazoline ring with spontaneous intramolecular attack of the imine nitrogen on the cyano carbon and bridging to a second Pd^{II} center (upon HCl elimination) to afford the final dimeric products **7**. They bear a previously unknown type of ligand, that is, a dihydropyrrolyl-iminoisoindolinone, and represent the first examples of complexes with such a ligand. The obtained Pd^{II} complexes **5** and **7** with the N-coordinated (pyrrolidinylidene)phthalamide and dihydropyrrolyl-iminoisoindolinone ligands, respectively, possess a remarkably high catalytic activity toward the Suzuki–Miyaura cross-coupling reaction, achieving the TOF value of $9\times10^{5}\,h^{-1}$.

We have thus developed synthetic strategies that involve cycloaddition reactions of a cyclic nitrone with conveniently substituted phthalonitriles, which provide access to novel multifunctional heterocyclic oxadiazoline, phthalamide, and iminoisoindolinone rings, with eventual significance for applications as dyes, pigments, or intermediates for the syntheses of pharmaceutical and naturally occurring compounds. The use of Pd^{II} complexes with such types of ligands as catalysts for C–C coupling reactions was demonstrated for particular cases and the extension to other related catalytic reactions appears to be rather promising and deserves to be explored.

Experimental Section

Material and instrumentation: Solvents and reagents were obtained from commercial sources (Aldrich) and used as received. The acyclic nitrone was synthesized by condensation of 4-methylbenzaldehyde and *N*-methylhydroxylamine, according to a published method.[24] For TLC, Merck Silica gel $60F_{254}$ plates have been used. C, H, and N elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. ^1H and ^{13}C spectra (in $CDCl_3$, $CDCl_3/CD_3OD$ or $[D_6]DMSO$) were measured on Bruker Avance II 300 and 400 MHz (UltraShield Magnet) spectrometers at ambient temperature. ^1H and ^{13}C chemical shifts (δ) are expressed in ppm relative to $SiMe_4$. J values are in Hz. Infrared spectra (4000–400 cm^{-1}) were recorded on a Bio-Rad FTS 3000 MX and a Jasco FTIR-430 instrument in KBr pellets and the wavenumbers are in cm^{-1}. Positive-ion FAB mass spectra were obtained on a Trio 2000 instrument by bombarding 3-nitrobenzyl alcohol (NBA) matrixes of samples with 8 keV (ca. 1.28×10^{15} J) Xe atoms. Electrospray mass spectra were carried out with an ion-trap instrument (Varian 500-MS LC Ion Trap Mass Spectrometer) equipped with an electrospray (ESI) ion source. For electrospray ionization, the drying gas and flow rate were optimized according to the particular sample with 35 p.s.i. nebulizer pressure. Scanning was performed from m/z 50 to 1500. The compounds were observed in the positive mode (capillary voltage = 80–105 V).

Reactions of phthalonitriles 1 (1a, $R^1=R^2=R^3=R^4=H$; 1b, $R^1=R^2=R^4=H$, $R^3=CH_3$; 1c, $R^1=R^4=H$, $R^2=R^3=Cl$; 1d, $R^1=R^2=R^3=R^4=Cl$; 1e, $R^1=R^2=R^3=R^4=F$) with the cyclic nitrone $^{-}O^{+}N{=}CHCH_2CH_2CMe_2$ 2: A solution of **1a** (50.0 mg, 0.390 mmol), **1b** (50.0 mg, 0.352 mmol), **1c** (50.0 mg, 0.254 mmol), **1d** (50.0 mg, 0.188 mmol) or **1e** (50.0 mg, 0.249 mmol) in $CHCl_3$ (4 mL) was added at room temperature to the nitrone **2** (2 equiv) and the mixture was heated at 80 °C in a sealed stainless steel tube for 12 h (**1a**, **1c**), 72 h (**1b**), 7 h (**1d**) or 3 h (**1e**) and the progress of the reaction was monitored by TLC. After evaporation of the solvent to dryness in vacuo, the crude residue was purified by column chromatography on silica (CH_2Cl_2) followed by evaporation of the solvent in vacuo to give the final products **3a**, **3b**, **4c**, **4d**, or **4e**, respectively.

Compound 3a: Yield: 49 %; ^1H NMR (300 MHz, $CDCl_3$): $\delta=7.77$–7.91 ppm (m, 4H, $CH_{aromatic}$); ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta=124.3$, 133.3 ($C_{aromatic}$), 135.0 ($C_{aromatic}$), 168.6 ppm (C=O); IR: $\tilde{\nu}=3448$ (ν(NH)), 1747 cm^{-1} (ν(C=O)); MS (FAB^+): m/z: 148 $[M+H]^+$; elemental analysis calcd (%) for $C_8H_5NO_2$: C 65.31, H 3.43, N 9.52; found: C 65.53, H 3.22, N 9.83.

Compound 3b: Yield: 51 %; ^1H NMR (300 MHz, $CDCl_3$): $\delta=2.53$ (s, 3H, CH_3), 7.55 (d, $J_{HH}=7.2$ Hz, 1H, $CH_{aromatic}$), 7.68 (s, 1H, $CH_{aromatic}$), 7.76 (d, $J_{HH}=7.2$ Hz, 1H, $CH_{aromatic}$), 8.09 ppm (s, br, 1H, NH); ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta=22.7$ (CH_3), 124.2, 124.7, 130.7, 133.7, 135.5 ($C_{aromatic}$), 146.3 ($C_{aromatic}$), 168.9 (C=O), 169.0 ppm (C=O); IR: $\tilde{\nu}=3212$ (ν(NH)), 1725 cm^{-1} (ν(C=O)); MS (FAB^+) m/z: 162 $[M+H]^+$; elemental analysis calcd (%) for $C_9H_7NO_2$: C 67.07, H 4.38, N 8.69; found: C 67.34, H 4.22, N 9.03.

Compound 4c: Yield: 65 %; ^1H NMR (300 MHz, $CDCl_3$): $\delta=1.23$ (s, 3H, CH_3), 1.35 (s, 3H, CH_3), 1.67–1.72 (m, 2H, CH_2), 2.09–2.15 (m, 1H,

CH_2), 2.30–2.35 (m, 1H, CH_2), 5.75 (dd, J_{HH} = 7.2, 2.4 Hz, 1H, NC*H*N), 7.87 (s, 1H, C$H_{aromatic}$), 8.09 ppm (s, 1H, C$H_{aromatic}$); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 23.9 (CH_3), 27.7 (CH_3), 31.9 (CH_2), 34.6 (CH_2), 69.9 (*C*(Me)$_2$), 92.2 (N*C*HN), 111.8 (N≡C), 116.1 (N≡C), 127.9, 132.5, 136.4, 136.5, 137.0 ($C_{aromatic}$), 138.6 ($C_{aromatic}$), 157.0 ppm (C=N); IR: $\tilde{\nu}$ = 2234 (ν(N≡C)), 1735 (ν(NCO), conjugated), 1648 cm^{-1} (C=N); MS (FAB$^+$): *m*/*z*: 310 [*M*]$^+$; elemental analysis calcd (%) for $C_{14}H_{13}N_3OCl_2$: C 54.21, H 4.22, N 13.55; found: C 54.56, H 4.15, N 13.12.

Compound 4d: Yield: 35%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.16 (s, 3H, CH_3), 1.39 (s, 3H, CH_3), 1.69–1.75 (m, 1H, CH_2), 1.89–1.99 (m, 1H, CH_2), 2.13–2.20 (m, 1H, CH_2), 2.25–2.35 (m, 1H, CH_2), 5.85 ppm (m, 1H, NC*H*N); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 23.7 (CH_3), 26.7 (CH_3), 31.9 (CH_2), 33.7 (CH_2), 70.3 (*C*(Me)$_2$), 92.5 (N*C*HN), 112.6 (N≡C), 114.0 (N≡C), 130.7, 133.3, 135.9, 136.7 ($C_{aromatic}$), 139.2 ($C_{aromatic}$), 154.9 ppm (C=N); IR: $\tilde{\nu}$ = 2239 (ν(N≡C)), 1742 (ν(NCO), conjugated), 1680 cm^{-1} (C=N); MS (FAB$^+$): *m*/*z*: 379 [*M*]$^+$; elemental analysis calcd (%) for $C_{14}H_{11}N_3OCl_4$: C 44.36, H 2.92, N 11.09; found: C 43.87, H 2.43, N, 10.74.

Compound 4e: Yield: 70%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.18 (s, 3H, CH_3), 1.34 (s, 3H, CH_3), 1.69–1.75 (m, 2H, CH_2), 2.07–2.16 (m, 1H, CH_2), 2.26–2.34 (m, 1H, CH_2), 5.76 ppm (dd, J_{HH} = 7.5, 2.7 Hz, 1H, NC*H*N); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 23.3 (CH_3), 26.8 (CH_3), 31.3 (CH_2), 33.6 (CH_2), 69.6 (*C*(Me)$_2$), 91.7 (N*C*HN), 109.3 (N≡C), 114.3 (N≡C), 140.4, 142.4, 145.0, 148.4, 151.7 ($C_{aromatic}$), 152.5 ($C_{aromatic}$), 162.3 ppm (C=N); IR: $\tilde{\nu}$ = 2242 (ν(N≡C)), 1739 (ν(NCO), conjugated), 1674 (ν(C=N)), 1628 cm^{-1} (ν(C=N)); MS (FAB$^+$) : *m*/*z*: 314 [*M*+H]$^+$; elemental analysis calcd (%) for $C_{14}H_{11}N_3OF_4$: C 53.68, H 3.54, N 13.41; found: C 53.72, H, 3.70, N 13.45.

Synthesis of compound 4e′: A solution of **1e** (50.0 mg, 0.249 mmol) in $CHCl_3$ (2 mL) was added at room temperature to the nitrone **2** (56.4 mg, 0.498 mmol) and the mixture was heated at 80 °C in a sealed tube for 16 h. After evaporation of the solvent to dryness in vacuo, the crude residue was purified as indicated above to give the corresponding product **4e′**.

Compound 4e′: Yield: 30%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.11 (s, 6H, two CH_3), 1.47 (s, 6H, two CH_3), 1.79–1.82 (m, 4H, two CH_2), 2.21–2.28 (m, 2H, CH_2), 2.44–2.53 (m, 2H, CH_2), 6.05 ppm (dd, J_{HH} = 12.9, 7.5 Hz, 2H, two NC*H*N); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 22.2 (CH_3), 28.4 (CH_3), 29.1 (CH_2), 36.6 (CH_2), 67.6 (*C*(Me)$_2$), 103.4 (N*C*HN), 145.3, 151.5 ($C_{aromatic}$), 153.1 ($C_{aromatic}$), 162.0 ppm (C=N); IR: $\tilde{\nu}$ = 1786 (ν(NCO), conjugated), 1728 (ν(NCO), conjugated), 1643 cm^{-1} (ν(C=N)); MS (FAB$^+$): *m*/*z*: 427 [*M*+H]$^+$; elemental analysis calcd for $C_{20}H_{22}N_4O_2F_4$: C 56.33, H 5.20, N 13.14; found: C 56.08, H 5.44, N 13.03.

Reactions of phthalonitriles 1 (1a, R^1 = R^2 = R^3 = R^4 = H; 1b, R^1 = R^2 = R^4 = H, R^3 = CH_3; 1c, R^1 = R^4 = H, R^2 = R^3 = Cl; 1d, R^1 = R^2 = R^3 = R^4 = Cl; 1e, R^1 = R^2 = R^3 = R^4 = F) with the cyclic nitrone $^-O^+N$=$CHCH_2CH_2CMe_2$ 2 in the presence of palladium(II) chloride ($PdCl_2$): A solution of **1a** (50.0 mg, 0.390 mmol), **1b** (50.0 mg, 0.352 mmol), **1c** (50.0 mg, 0.254 mmol), **1d** (50.0 mg, 0.188 mmol), or **1e** (50.0 mg, 0.249 mmol) in acetone (8 mL) was added at room temperature to the nitrone **2** (2 equiv) and palladium chloride (1 equiv), and the mixture was stirred at room temperature for 12 h. During the course of the reaction, the brown $PdCl_2$ powder dissolved, forming a homogeneous light yellow solution. The reaction mixture was then dried in vacuo, washed with three 10 mL portions of diethyl ether and dried under air. The final complex **5** was recrystallized from acetone.

Compound 5a: Yield: 75%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.48 (s, 6H; two CH_3), 1.59 (s, 6H; two CH_3), 2.11 (t, J_{HH} = 7.2 Hz, 4H; two CH_2), 3.45 (t, J_{HH} = 7.2 Hz, 4H; two CH_2), 7.68 (s, br, 4H; C$H_{aromatic}$), 10.73 ppm (s, br, 2H; NH); ^{13}C NMR (75.4 MHz, $CDCl_3$ + CD_3OD): δ = 27.6 (CH_3), 30.5 (CH_3), 33.7 (CH_2), 36.4 (CH_2), 64.8 (*C*(Me)$_2$), 128.8, 131.2 ($C_{aromatic}$), 135.6 ($C_{aromatic}$), 169.5 (NC=N), 173.4 ppm (NC=O); IR: $\tilde{\nu}$ = 3285 (ν(NH)), 3237 (ν(NH)), 1712 (ν(NC=O)), 1657 (ν(NC=N), conjugated), 1591 cm^{-1} (ν(NC=N), conjugated); MS (FAB$^+$): *m*/*z*: 554 [*M*+Na]$^+$, 531 [*M*]$^+$, 495 [*M*−Cl]$^+$, 459 [*M*−2Cl]$^+$; elemental analysis calcd for $C_{20}H_{26}N_4O_2Cl_2Pd$: C 45.17, H 4.93, N 10.54; found: C 44.77, H 4.83, N 10.61.

Compound 5b: Yield: 73%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.42 (s, 6H, two CH_3), 1.44 (s, 6H, two CH_3), 2.11 (t, J_{HH} = 7.3 Hz, 4H, two CH_2), 2.45 (s, 3H, CH_3Ph), 3.47 (t, J_{HH} = 7.3 Hz, 4H, two CH_2), 7.42–7.58 (m, 3H, C$H_{aromatic}$), 10.67 ppm (s, br, 2H, NH); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 21.3 (*C*H$_3$Ph), 25.2 (CH_3), 28.3 (CH_3), 30.8 (CH_2), 33.9 (CH_2), 73.6 (*C*(Me)$_2$), 129.4, 129.5, 132.1, 133.1, 135.9 ($C_{aromatic}$), 142.0 ($C_{aromatic}$), 174.1 ppm (NC=O); IR: $\tilde{\nu}$ = 3433 (ν(NH)), 3276 (ν(NH)), 1643, 1631 (ν(NC=N) and ν(NC=O), conjugated), 1589 cm^{-1} (ν(NC=N) and (ν(NC=O), conjugated); MS (ESI): *m*/*z*: 547 [*M*+H]$^+$; elemental analysis calcd for $C_{21}H_{28}Cl_2N_4O_2Pd$: C 46.21, H 5.17, N 10.27; found: C 46.52, H 5.13, N 10.16.

Compound 5c: Yield: 80%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.44 (s, 6H, two CH_3), 1.50 (s, 6H, two CH_3), 2.07–2.14 (m, 4H, two CH_2), 2.56–2.61 (m, 2H, CH_2), 3.41–3.52 (m, 2H, CH_2), 7.76 (s, 2H, C$H_{aromatic}$), 10.61 ppm (s, br, 2H, NH); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 25.3 (CH_3), 28.3 (CH_3), 30.9 (CH_2), 34.0 (CH_2), 131.2, 134.9 ($C_{aromatic}$), 136.1 ($C_{aromatic}$), 174.5 (NC=O); IR: $\tilde{\nu}$ = 3250 (ν(NH)), 1789 (ν(NC=O)), 1670 (ν(NC=N), conjugated), 1600 cm^{-1} (ν(NC=N), conjugated); MS (FAB$^+$) *m*/*z*: 601 [*M*+H]$^+$, 623 [*M*+Na]$^+$, 565 [*M*−Cl]$^+$; elemental analysis calcd for $C_{20}H_{24}N_4O_2Cl_4Pd$: C 39.99, H 4.03, N 9.33; found: C 40.14, H 4.00, N 9.39; the poor solubility of the complex did not allow the acquisition of all the ^{13}C signals.

Compound 5d: Yield: 85%; ^{1}H NMR (400 MHz, $CDCl_3$ + CD_3OD): δ = 1.14 (s, 6H, two CH_3), 1.20 (s, 6H, two CH_3), 1.85 (t, J_{HH} = 6.3, 4H, two CH_2), 2.70 ppm (t, J_{HH} = 6.3 Hz, 4H, two CH_2); ^{13}C NMR (100.6 MHz, $CDCl_3$ + CD_3OD): δ = 23.5 (CH_3), 27.5 (CH_3), 30.9 (CH_2), 34.8 ppm (CH_2); IR: $\tilde{\nu}$ = 3322 (ν(NH)), 1793 (ν(NC=O), conjugated), 1737 (ν(NC=O), conjugated), 1686 cm^{-1} (ν(NC=N)); MS (FAB$^+$): *m*/*z*: 635 [*M*−Cl]$^+$; elemental analysis calcd for $C_{20}H_{22}N_4O_2Cl_6Pd$: C 35.88, H 3.31, N 8.37; found: C 35.44, H 3.42, N 8.48. The poor solubility of the complex did not allow the acquisition of all the NMR data.

Compound 5e: Yield: 90%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.37 (s, 6H, two CH_3), 1.41 (s, 6H, two CH_3), 2.03 (m, 4H, two CH_2), 2.55 (m, 2H, CH_2), 3.74 (m, 2H, CH_2), 10.73 ppm (s, br, 2H, NH); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 25.1 (CH_3), 27.8 (CH_3), 33.7 (CH_2), 35.1 (CH_2), 73.5 (*C*(Me)$_2$), 140.1, 142.8 ($C_{aromatic}$), 146.2 ($C_{aromatic}$), 168.6 (C=N), 174.1 (NC=O); IR: $\tilde{\nu}$ = 3339 (ν(NH)), 1788 (ν(NC=O), conjugated), 1704 (ν(NC=O), conjugated), 1650 (ν(NC=N), conjugated), 1588 cm^{-1} (ν(NC=N), conjugated); MS (FAB$^+$): *m*/*z*: 605 [*M*+H]$^+$; elemental analysis calcd for $C_{20}H_{22}N_4O_2F_4Cl_2Pd$: C 39.79, H 3.67, N 9.28; found: C 40.01, H 3.76, N 9.40.

Synthesis of intermediates 6 and of the dimers 7: Palladium chloride (1 eq) was added to a solution of **4c** (50.0 mg, 0.161 mmol) or **4e** (50.0 mg, 0.159 mmol) in acetone (8 mL) at room temperature and the mixture was stirred a) at room temperature until full dissolution of $PdCl_2$ was observed (ca. 12 h) to give intermediates **6** or b) under reflux for 48 h or at room temperature for 72 h to give dimers **7**. During the course of the reaction, the brown $PdCl_2$ powder dissolved, forming a homogeneous light yellow solution. In case a), the reaction mixture is then evaporated to dryness in vacuo, washed with three 10 mL portions of diethyl ether and dried under air (for **6c**) or directly analyzed by ESI MS (for **6e**). In case b), after formation of the yellow solution, a yellow precipitate separates out. It was then filtered off, washed with acetone (3×10 mL) and dried under air (**7**).

Compound 6c: Yield: 34%; ^{1}H NMR (300 MHz, $CDCl_3$ + CD_3OD): δ = 1.15 (s, 6H, two CH_3), 1.42 (s, 6H, two CH_3), 1.70–1.79 (m, 4H, two CH_2), 1.86–1.97 (m, 2H, CH_2), 2.37–2.45 (m, 2H, CH_2), 5.55 (dd, J_{HH} = 6.2 and 2.7 Hz, 2H, NC*H*N), 7.89 (s, 2H, C$H_{aromatic}$), 9.25 ppm (s, 2H, C$H_{aromatic}$); ^{13}C NMR (75.4 MHz, $CDCl_3$ + CD_3OD): δ = 22.7 (CH_3), 26.2 (CH_3), 31.1 (CH_2), 33.5 (CH_2), 71.4 (*C*(Me)$_2$), 89.7 (N*C*HN), 111.9 (N≡C), 114.7 (N≡C), 126.4, 133.6, 133.7, 135.6, 138.0 ($C_{aromatic}$), 138.2 ($C_{aromatic}$), 161.6 ppm (C=N); IR: $\tilde{\nu}$ = 2240 (ν(C=N)), 1670, 1642 cm^{-1} (ν(OC=N), conjugated); MS (ESI in acetone): *m*/*z*: 799 [*M*+H]$^+$; elemental analysis calcd for $C_{28}H_{26}Cl_6N_6O_2Pd$: C 42.16, H 3.29, N 10.54; found: C 42.21, H 3.26, N 10.57.

Compound 6e: MS (ESI): (of the reaction mixture after 12 h of stirring at room temperature), *m*/*z*: 805 [*M*+1]$^+$, 732 [*M*−2Cl-1]$^+$.

Compound 7c: Yield: 70%; ^{1}H NMR (400 MHz, [D_6]DMSO): δ = 1.64 (s, 12H, four CH_3), 1.93 (t, J_{HH} = 6.0 Hz, 4H, two CH_2), 3.22 (t, J_{HH} = 6.0 Hz, 4H, two CH_2), 8.34 (s, 2H, C$H_{aromatic}$), 9.04 ppm (s, 2H, C$H_{aromatic}$); ^{13}C

NMR (100.6 MHz, [D$_6$]DMSO), δ = 27.5 (CH_3), 33.4 (CH_2), 75.0 (C(Me)$_2$), 127.0, 127.3, 129.6, 129.9, 138.3 and 139.2 ($C_{aromatic}$), 161.0 (NC=N), 163.8 ppm (NC=N, NC=O, conjugated); IR: $\tilde{\nu}$ = 1776 (ν(NC=O), conjugated), 1687 (ν(NC=N), conjugated); MS (ESI, DMSO): m/z: 903 $[M+H]^+$; elemental analysis calcd for $C_{28}H_{24}Cl_6N_6O_2Pd_2$: C 37.28, H 2.68, N 9.32; found: C 37.56, H 2.58, N 9.12. Crystals of **7c** were prepared by slow evaporation of its methanol/chloroform solution.

Compound 7e: Yield: 75%; ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 1.56 (s, 12H, four CH_3), 1.95 (t, J_{HH} = 8.0 Hz, 4H; two CH_2), 3.11 ppm (t, J_{HH} = 8.0 Hz, 4H; two CH_2); ^{13}C NMR (100.6 MHz, [D$_6$]DMSO), δ: 27.5 (CH_3), 32.4 (CH_2), 38.9 (CH_2), 76.5 (C(Me)$_2$), 148.4 (C–$F_{aromatic}$), 159.8 (NC=N), 162.1 ppm (NC=O, conjugated); IR: $\tilde{\nu}$ = 1787 (ν(NC=O), conjugated), 1707 cm^{-1} (ν(NC=N), conjugated); MS (ESI, DMSO): m/z: 909 $[M+H]^+$; elemental analysis calcd for $C_{28}H_{20}Cl_2F_8N_6O_2Pd_2$: C 37.03, H 2.22, N 9.25; found: C 37.56, H 2.18, N 9.38. The poor solubility of the complex did not allow collection of all the ^{13}C signals.

Attempts to react 4 with nucleophiles other than the cyclic nitrone 2 in the presence of palladium(II) chloride: Compound **4c** (20.0 mg, 0.064 mmol) or **4e** (20.1 mg, 0.064 mmol) was dissolved in acetone, whereupon $PdCl_2$ (11.4 mg, 0.064 mmol) and the nucleophile (0.064 mmol) (Me$_2$C=NOH, $^-$O$^+$N(Me)=C(H)(C$_6$H$_4$Me-4) or Et$_2$NOH) were added. Continuous stirring at room temperature for 72 h led to a yellow precipitate, which, by IR and NMR spectroscopic analyses, was shown to be the corresponding dimer **7**. Evaporation of the separated solution gave a yellow oil, the main component of which was also the dimer **7**, contaminated with as yet unidentified species.

Liberation of the ketoimine 5e′ from the complex 5e: Dppe (72.6 mg, 0.182 mmol) was added to a solution of **5e** (55.0 mg, 0.091 mmol) in $CDCl_3$ (2 mL) and the mixture was allowed to stand at 40°C for 30 min, whereupon colorless [PdCl$_2$(dppe)] precipitated. This precipitate was separated by filtration and identified by ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 55.9 (56.7) ppm[22]). The free ketoimine **5e′** was characterized in solution by NMR spectroscopy.

Compound 5e′: Yield: 50%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.29 (s, 6H, two CH_3), 1.42 (s, 6H, two CH_3), 1.89 (t, J_{HH} = 7.2 Hz, 4H, two CH_2), 2.84 (t, J_{HH} = 7.2 Hz, 4H, two CH_2), 7.55 ppm (s, br, 2H, NH); ^{13}C NMR (100.6, $CDCl_3$): δ = 25.3 (CH_3), 28.0 (CH_3), 34.0 (CH_2), 35.3 (CH_2), 73.4 (C(Me)$_2$), 139.8, 141.5 ($C_{aromatic}$), 145.1 ($C_{aromatic}$), 169.1 (C=N), 172.4 ppm (NC=O); IR: $\tilde{\nu}$ = 3438 (ν(NH)), 1739 (ν(NC=O), conjugated), 1699 (ν(NC=O), conjugated), 1629 cm^{-1} (ν(NC=N), conjugated); MS (ESI): m/z: 427 $[M+H]^+$; elemental analysis calcd for $C_{20}H_{22}F_4N_4O_2$: C 56.33, H 5.20, N 13.14; found: C 56.67, H 4.99, N 13.50.

Catalytic Suzuki–Miyaura cross coupling reactions of bromobenzene and phenylboronic acid: A 100 mL round-bottom flask was charged with bromobenzene (0.785 g, 5.00 mmol), phenylboronic acid (0.73 g, 6.0 mmol), potassium carbonate (1.38 g, 10.0 mmol), 1 mL of a freshly prepared (see below) acetone solution of catalyst **5a** or **7c** containing 5×10^{-4}–5×10^{-6} mmol of the complex (10^{-2}–10^{-4} mol% Pd relative to bromobenzene), and toluene (50 mL). The solution was stirred at 100°C in air, and the reaction progress was monitored by TLC (hexane/CH_2Cl_2 10:1). After completion, the reaction mixture was poured into water (excess) and extracted with dichloromethane (3×25 mL). The organic extract was dried with $MgSO_4$ and evaporated in vacuo and the crude residue was purified by column chromatography on silica (hexane/CH_2Cl_2 10:1). Evaporation of the solvent in vacuo afforded the biphenyl product in 90–95% yield (pure by ^{1}H and ^{13}C NMR).

The preparation of the catalyst solution was as follows: Catalyst **5a** or **7c** (5×10^{-3} mmol, 2.65 mg or 4.50 mg of **5a** or **7c**, respectively) was dissolved in acetone (10 mL). By subsequent dilutions, solutions containing 5×10^{-4} and 5×10^{-5} mmol in acetone (10 mL) (that is, with concentrations of 5×10^{-5} and 5×10^{-6} M, respectively) were prepared.

X-ray crystal structure determinations: The X-ray quality single crystals of **4c**, **5a**, **5c**, and **7c** were grown by slow evaporation at room temperature of their $CHCl_3$ (for **4c** and **5a**) or $CHCl_3$/MeOH (for **5c** and **7c**) solutions. They were mounted in inert oil within the cold N_2 stream of the diffractometer. Intensity data were collected by using a Bruker AXS-KAPPA APEX II diffractometer using graphite monochromated $Mo_{K\alpha}$ radiation. Data were collected at 150 K using omega scans of 0.5° per frame and a full sphere of data was obtained. Cell parameters were retrieved using Bruker SMART software and refined using Bruker SAINT on all the observed reflections. Absorption corrections were applied using SADABS. Structures were solved by direct methods by using the SHELXS-97 package[25] and refined with SHELXL-97[26] with the WinGX graphical user interface.[27] All hydrogens were inserted in calculated positions.

There are disordered solvents present in structures **5c** and **7c**. Attempts were made to model these but were unsuccessful since there were no obvious site occupations for the solvent molecules. PLATON/SQUEEZE[28] was used to correct the data. Potential solvent volumes of 558 (**5c**) or 324 (**7c**) Å^3 were found and 64 (**5c**) or 158 (**7c**) electrons per unit cell worth of scattering were located in the voids. The electron counts suggested the presence of ca. one additional water molecule per unit cell in **5c**, and one molecule of acetone and one molecule of water in **7c**.

The crystallographic details for **4c**, **5a**, **5c** and **7c** are summarized in Table 2. CCDC-681281, CCDC-681282, CCDC-681283, and CCDC-681284 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 2. Crystal data and structure refinement details for compounds **4c**, **5a**, **5c**, and **7c**.

	4c	**5a**·$CHCl_3$	**5c**·C_3H_6O·H_2O	**7c**·2 $CHCl_3$
empirical formula	$C_{14}H_{13}N_3OCl_2$	$C_{20}H_{26}N_4O_2Cl_2Pd$	$C_{20}H_{24}N_4O_2Cl_4Pd$	$C_{28}H_{24}Cl_6N_6O_2Pd_2$·2$CHCl_3$
M_r	310.17	651.14	676.75	1140.81
T [K]	150(2)	150(2)	150(2)	150(2)
λ [Å]	0.71069	0.71069	0.71069	0.71069
crystal system	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$I2/a$	$C2/c$
a [Å]	16.753(2)	13.3550(11)	21.5056(13)	11.6758(14)
b [Å]	6.3621(6)	14.8346(11)	12.6768(8)	17.012(2)
c [Å]	14.428(3)	15.0941(10)	22.3470(18)	21.064(3)
β [°]	113.704(4)	122.999(3)	102.571(3)	100.580(5)
V [Å^3]	1408.1(4)	2508.0 (3)	5946.2(7)	4112.7(9)
Z	4	4	4	4
ρ_{calcd} [Mg m^{-3}]	1.463	1.724	1.512	1.842
μ($Mo_{K\alpha}$) [mm^{-1}]	0.459	1.300	1.018	1.692
no. of collected reflections	7379	13623	37425	7824
no. of unique reflections	2385	4387	5417	3649
R_1[a] ($I\geq2\sigma$)	0.0426	0.0621	0.0318	0.0465
wR_2[b] ($I\geq2\sigma$)	0.0947	0.1438	0.0700	0.1171

[a] $R_1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b] $wR_2=[\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

Acknowledgements

This work has been partially supported by the Fundação para a Ciência e a Tecnologia (FCT) and its POCI 2010 program (FEDER funded) (Portugal). J. L. and M. N. K. express gratitude to FCT for their post-doc fellowships (grants SFRH/BPD/20927/2004 and SFRH/BPD/14465/2003), and to the FCT and the Instituto Superior Técnico (IST) for a research contracts (Ciência 2007 program). Thanks are also due to Dr. M. C. Vaz (microanalytic service), Dr. C. Oliveira and Dr. K. Koci (ESI MS) and Mr. I. Marques (FAB MS) for the analytical services.

[1] a) G. Desimoni, G. Faita, K. A. Jorgensen, *Chem. Rev.* **2006**, *106*, 3561; b) H. A. McManus, P. J. Guiry, *Chem. Rev.* **2004**, *104*, 4151; c) A. J. Phillips, A. D. Abell, *Aldrichimica Acta* **1999**, *32*, 75.

[2] a) D. Lednicer, *New Drug Discovery and Development*, Wiley, **2007**; b) *Drug Discovery and Development*, (Ed.: M. S. Chorghade), Wiley, **2006**.

[3] a) *The Chemistry of β-Lactams*, (Ed.: M. I. Page), Chapman and Hall, London, **1997**; b) A. Chimirri, S. Grasso, A.-M. Montforte, A. Rao, M. Zappala, *Farmaco* **1996**, *51*, 125.

[4] a) N. B. McKeown, "*Phthalocyanines*", in: *Comprehensive Coordination Chemistry II Vol. 1*, 2nd ed. (Ed.: A. B. P. Lever), Elsevier, Amsterdam, **2003**, Chapter 1.24.and references therein; b) *Phthalocyanines. Properties and Applications Vols. 1–4*, (Eds.: C. C. Leznoff, A. B. P. Lever) Wiley, Weinheim **1982**, **1989**, **1993**, **1996**.

[5] P. Gregory, "*Metal Complexes as Speciality Dyes and Pigments*", in *Comprehensive Coordination Chemistry II Vol. 9*, 2nd ed., (Ed. A. B. P., Lever), Elsevier, Amsterdam, **2003**, Chapter 9.12. and references therein.

[6] a) A. S. Polo, M. K. Itokazu, K. M. Frin, A. O. de Toledo Patrocínio, N. Y. Murakami Iha, *Coord. Chem. Rev.* **2006**, *250*, 1669; b) B. Higgins, B. A. DeGraff, J. N. Demas, *Inorg. Chem.* **2005**, *44*, 6662; c) J.-M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*, Wiley, Weinheim, **1995**.

[7] a) L. X. Yin, J. Liebscher, *Chem. Rev.* **2007**, *107*, 133; b) *Metal-catalyzed Cross-coupling Reactions*, (Eds.: F. Diederich, P. J. Stang), Wiley, Weinheim, **2001**; c) J. Tsuji, *Palladium Reagents and Catalysts-Innovations in Organic Synthesis*, Wiley, Chichester, **1997**.

[8] a) S. Kobayashi, K. A. Jorgensen, *Cycloaddition Reactions in Organic Synthesis*, Wiley, Weinheim, **2002**; b) K. V. Gothelf, K. A. Jorgensen, *Chem. Rev.* **1998**, *98*, 863; c) K. V. Gothelf, K. A. Jorgensen, *Chem. Commun.* **2000**, 1449.

[9] a) V. Yu. Kukushkin, A. J. L. Pombeiro, *Chem. Rev.* **2002**, *102*, 1771; b) R. A. Michelin, M. Mozzon, R. Bertani, *Coord. Chem. Rev.* **1996**, *147*, 299.

[10] N. A. Bokach, A. A. Krokhin, A. A. Nazarov, V. Yu. Kukushkin, M. Haukka, J. J. R. Fraústo da Silva, A. J. L. Pombeiro, *Eur. J. Inorg. Chem.* **2005**, 3042.

[11] a) J. Lasri, M. A. Charmier Januário, M. F. C. Guedes da Silva, A. J. L. Pombeiro, *Dalton Trans.* **2007**, 3259; b) J. Lasri, M. A. Charmier Januário, M. Haukka, A. J. L. Pombeiro, *J. Org. Chem.* **2007**, *72*, 750; c) M. A. Charmier Januário, V. Yu. Kukushkin, A. J. L. Pombeiro, *Dalton Trans.* **2003**, 2540; d) G. Wagner, M. Haukka, J. J. R. Fraústo da Silva, A. J. L. Pombeiro, V. Yu. Kukushkin, *Inorg. Chem.* **2001**, *40*, 264; e) G. Wagner, A. J. L. Pombeiro, V. Yu. Kukushkin, *J. Am. Chem. Soc.* **2000**, *122*, 3106.

[12] M. A. Charmier Januário, M. Haukka, A. J. L. Pombeiro, *Dalton Trans.* **2004**, 2741.

[13] a) I. Ando, T. Ohtsuka, N. Miki, T. Takahashi, Y. Hayase, Y. Hayashi, *Agric. Biol. Chem.* **1989**, *53*, 2001; b) Yu. S. Andreichikov, V. V. Zalesov, N. A. Podushkina, *Pharm. Chem. J.* **1980**, *14*, 99; c) J.-J. Lu, H. L. Wehrmeister, US-A 4694016, **1987**; d) A. Guidi, F. Pasqui, M. Almatura, C. A. Maggi, WO/2002/020437, **2002**; e) K. Sakata, M. Morimoto, H. Kodama, T. Nishimatsu, WO/2002/087334, **2002**.

[14] a) D. Dallinger, C. O. Kappe, *Chem. Rev.* **2007**, *107*, 2563; b) E. A. B. Kantchev, C. J. O'Brien, M. G. Organ, *Angew. Chem.* **2007**, *119*, 2824; *Angew. Chem. Int. Ed.* **2007**, *46*, 2768; c) J. Hassan, M. Se′vignon, C. Gozzi, E. Schulz, M. Lemaire, *Chem. Rev.* **2002**, *102*, 1359; d) S. Kotha, K. Lahiri, D. Kashinath, *Tetrahedron* **2002**, *58*, 9633; e) N. Miyaura, A. Suzuki, *Chem. Rev.* **1995**, *95*, 2457.

[15] K. B. G. Torssell, *Nitrile Oxides, Nitrones, and Nitronates in Organic Synthesis*, Wiley, **1988**.

[16] K. V. Luzyanin, V. Yu. Kukushkin, M. N. Kopylovich, A. A. Nazarov, M. Galanski, A. J. L. Pombeiro, *Adv. Synth. Catal.* **2008**, *350*, 135.

[17] a) E. S. H. El Ashry, Y. El Kilany, N. Rashed, H. Assafir, *Adv. Heterocycl. Chem.* **2000**, *75*, 79; b) J. Liebscher, A. Hassoun, H. van der Plas, C. Stam, *J. Heterocycl. Chem.* **1990**, *27*, 1441.

[18] a) L. Eberson, J. J. McCullough, C. M. Hartshorn, M. P. Hartshorn, *J. Chem. Soc. Perkin Trans. 2* **1998**, *1*, 41; b) L. Eberson, C. M. Hartshorn, M. P. Hartshorn, J. J. McCullough, *Synth. Commun.* **1997**, *27*, 3779; c) L. A. G. M. Van den Broek, *Tetrahedron* **1996**, *52*, 4467; d) H. Sang, E. G. Janzen, L. Poyer, *J. Chem. Soc. Perkin Trans. 2* **1996**, *6*, 1183; e) Y. Yu, N. Watanabe, M. Ohno, S. Eguchi, *J. Chem. Soc. Perkin Trans. 1* **1995**, *11*, 1417; f) Y. Yu, H. Fujita, M. Ohno, S. Eguchi, *Synthesis* **1995**, 498; g) Y. Yu, M. Ohno, S. Eguchi, *J. Chem. Soc. Chem. Commun.* **1994**, 331; h) P. H. H. Hermkens, J. H. van Maarseveen, C. G. Kruse, H. W. Scheeren, *Tetrahedron* **1988**, *44*, 6491; i) R. Plate, P. H. H. Hermkens, J. M. M. Smits, R. J. F. Nivard, H. C. J. Ottenheijm, *J. Org. Chem.* **1987**, *52*, 1047.

[19] F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, *J. Chem. Soc. Perkin Trans. 2*, **1987**, S1-S19.

[20] a) M. N. Kopylovich, M. Haukka, A. M. Kirillov, V. Yu. Kukushkin, A. J. L. Pombeiro, *Chem. Eur. J.* **2007**, *13*, 786; b) M. N. Kopylovich, V. Yu. Kukushkin, M. Haukka, K. V. Luzyanin, A. J. L. Pombeiro, *J. Am. Chem. Soc.* **2004**, *126*, 15040.

[21] a) B. Desai, T. N. Danks, G. Wagner, *Dalton Trans.* **2003**, 2544; b) G. A. Anderson, M. Lin, *Inorg. Synth.* **1990**, *28*, 60; c) M. A. Andrews, T. C. T. Chang, C. W. F. Cheng, T. J. Emge, K. P. Kelly, T. F. Koetzle, *J. Am. Chem. Soc.* **1984**, *106*, 5913.

[22] a) N. A. Bokach, V. Yu. Kukushkin, M. Haukka, A. J. L. Pombeiro, *Eur. J. Inorg. Chem.* **2005**, 845; b) P. S. Jarrett, O. M. Ni Dhubhghaill, P. J. Sadler, *J. Chem. Soc. Dalton Trans.* **1993**, 1863.

[23] a) L. Ray, M. N. Shaikh, P. Ghosh, *Organometallics* **2007**, *26*, 958; b) L. Braun, P. Liptau, G. Kehr, J. Ugolotti, R. Frohlich, G. Erker, *Dalton Trans.* **2007**, 1409; c) H. Hagiwara, K. H. Ko, T. Hoshi, T. Suzuki, *Chem. Commun.* **2007**, 2838; d) Q. Luo, S. Eibauer, O. Reiser, *J. Mol. Cat. A* **2007**, *268*, 65; e) J. K. Eberhardt, R. Fröhlich, E.-U. Würthwein, *J. Org. Chem.* **2003**, *68*, 6690.

[24] D. Döpp, H. Döpp, in: *Houben-Weyl Methoden der Organischen Chemie Vol. E14b, part 2*, (Eds.: D. Klamann, H. Hagemann), Thieme, Stuttgart, Germany, **1990**, 1372.

[25] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **1990**, *46*, 467.

[26] G. M. Sheldrick, SHELXL-97, University of Gottingen, Germany, 1997.

[27] L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837.

[28] A. L. Spek, *Acta Crystallogr. Sect. A* **1990**, *46*, C34.

Received: March 19, 2008
Published online: August 26, 2008

