Synthesis of (1,2,4-Oxadiazole)palladium(II) Complexes by [2 + 3] Cycloaddition of Nitrile Oxides to Organonitriles in the Presence of $PdCl_2$

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Keywords: Palladium / 1,2,4-oxadiazole complexes / Nitrile complexes / Nitrile oxide complexes / Cycloaddition

The reaction between the nitrile oxides 2,4,6-$R'_3C_6H_2CNO$ (R′ = Me, OMe) and *trans*-$[PdCl_2(RCN)_2]$, or RCN (R = Me, Et, CH_2CN, NMe_2, Ph) in the presence of $PdCl_2$, proceeded smoothly under mild conditions and allowed the isolation of the 1,2,4-oxadiazole complexes *trans*-$[PdCl_2\{N^a{=}C(R)\text{-}ON{=}C^b(C_6H_2R'_3)(N^a\text{–}C^b)\}_2]$ (**1**–**8**) in 40–85 % yields. In CH_2Cl_2, the reaction between 2,4,6-$R'_3C_6H_2CNO$ and $[PdCl_2(MeCN)_2]$ furnishes $[PdCl_2(ONCC_6H_2R'_3)_2]$ (**9** and **10**), which are the first representatives of metal compounds where nitrile oxides act as ligands. The 1,2,4-oxadiazole complexes **1**–**8** were characterized by elemental analysis, FAB mass spectrometry, and IR, ^1H and $^{13}C\{^1H\}$ NMR spectroscopy, while **2**, **3**, **7**, and **8** were additionally characterized by X-ray crystallography. The liberation of the heterocyclic species from **1**–**8** was successfully performed by substitution reaction either with 1,2-bis(diphenylphosphanyl)ethane or with an excess amount of $Na_2S·7H_2O$ in MeOH; the liberated 1,2,4-oxadiazoles (**11**–**18**) were characterized by positive-ion FAB mass spectrometry and ^1H and $^{13}C\{^1H\}$ NMR spectroscopy.

Introduction

1,2,4-Oxadiazoles are an important class of ring systems containing one O and two N atoms.[1] These compounds have widespread applications in biology and medicine insofar as some of them exhibit intrinsic analgesic,[2] anti-inflammatory,[3] and anti-picornaviral[4] effects and show high efficacy as agonists[5] and antagonists[6] for different receptors. Other areas of research in the chemistry of 1,2,4-oxadiazoles include plant protection,[7] their use as liquid-crystalline mesophases,[8] dyeing or printing with 1,2,4-oxadiazole azo dyes,[9] and they are also constituents of fluorescent whiteners.[10] Despite the wealth of chemistry associated with 1,2,4-oxadiazoles in general, the coordination chemistry of these heterocycles has so far been little explored,[11] although the opposite holds true for the *isomeric* 1,3,4-oxadiazoles. Complexes of the latter have been intensively investigated as angular bridging ligands that give unusual coordination polymers[12] and binuclear complexes.[13] In addition, metal complexes with 1,3,4-oxadiazole-derived ligands exhibit important luminescent,[14] electroluminescent,[15] liquid crystal,[16] and magnetic properties.[17]

As a continuation of our project on [2 + 3] cycloadditions[18,19] of dipoles to metal-activated nitriles[20,21] to give heterocyclic systems, we have studied a [2 + 3] cycloaddition of nitrile oxides to nitriles in the presence of a Pd^{II} center and isolated a family of previously unknown (1,2,4-oxadiazole)palladium(II) species. We also observed that the reaction between the nitrile oxides and $[PdCl_2(MeCN)_2]$ in CH_2Cl_2 (instead of MeCN) led to the first representatives of nitrile oxide metal compounds. All these results are reported in this work.

Results and Discussion

Preparation of (1,2,4-Oxadiazole)palladium(II) Complexes

Recently we have studied the reaction of $[PtCl_4(RCN)_2]$ with the nitrile oxides 2,4,6-$R'_3C_6H_2CNO$ which, after [2 + 3] cycloaddition, gives the (1,2,4-oxadiazole)platinum(IV) complexes $[PtCl_4\{N^a{=}C(R)ON{=}C^bC_6H_2R'_3(N^a\text{–}C^b)\}_2]$.[19] This reaction opens up an easy route to 1,2,4-oxadiazole metal complexes and also allows the preparation of the heterocycles, after liberation of the ligands, under mild conditions. This method to achieve 1,2,4-oxadiazole complexes has been applied here to Pd^{II} systems to obtain a family of previously unknown 1,2,4-oxadiazole complexes.

As dipolarophiles for this study we used the nitrile and dialkylcyanamide palladium(II) complexes *trans*-$[PdCl_2(RCN)_2]$ because it has been shown[20,21] that the Pd^{II}

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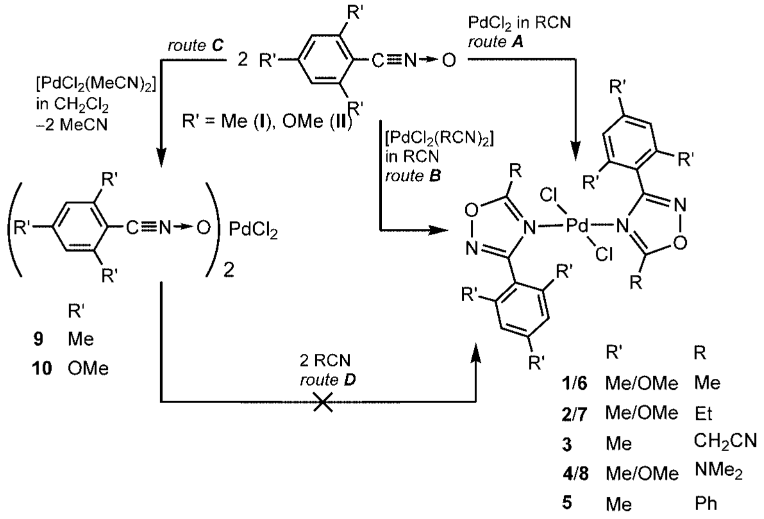
DOI: 10.1002/ejic.200400580



Scheme 1

center strongly activates the ligated nitriles toward the addition of various *nucleophiles* and this type of reactivity can model,[22] to some extent, the [2 + 3] cycloaddition of *dipoles*. Two relatively stable aryl nitrile oxides, i.e. 2,4,6-$Me_3C_6H_2CNO$ (**I**) and 2,4,6-$(MeO)_3C_6H_2CNO$ (**II**),[23] were chosen as dipoles.

In agreement with our expectations, the cycloaddition of **I** or **II** to nitriles in *trans*-$[PdCl_2(RCN)_2]$ to achieve 1,2,4-oxadiazole metal species proceeded smoothly and gave the complexes *trans*-$[PdCl_2\{N^a{=}C(R)ON{=}C^b(C_6H_2R'_3)(N^a\text{–}C^b)\}_2]$ (**1**–**8**) in 40–85% yields. The reaction was performed by two rather similar, albeit technically distinct, routes (Scheme 1). In the first route (**A**), both $PdCl_2$ and the nitrile oxide **I** or **II** (3–4 equiv.) were reacted in a suspension of neat nitrile RCN (R = Me, Et, NMe_2, Ph) or, in the case of the solid malonodinitrile (R = CH_2CN) (sixfold molar excess vs. $PdCl_2$), in a CH_2Cl_2 solution. In the second route (**B**), the nitrile complexes *trans*-$[PdCl_2(RCN)_2]$ (R = Me, Et, Ph), dissolved in the corresponding nitrile, were treated with the nitrile oxides **I** or **II** (3–4 equiv.). In both routes the reaction was performed at 40 °C for 12–18 h and the isolated yields for every particular compound, prepared by the two methods, are almost the same. The isolation of the (1,2,4-oxadiazole)palladium(II) products failed only in the case of treatment of the less-reactive (towards the cycloaddition, but more reactive towards the substitution; see below) nitrile oxide **II** with the reactive (but weak ligand) nitriles PhCN and $NCCH_2CN$ at the Pd^{II} center; this reaction gives a mixture of products.

Reaction of $PdCl_2$ with neat RCN is well known and is commonly applied for the preparation of the complexes *trans*-$[PdCl_2(RCN)_2]$.[24] Hence, it is not surprising that the reaction rate and the isolated yields are similar for both routes, because route **A** conceivably includes the formation of $[PdCl_2(RCN)_2]$, upon dissolution of $PdCl_2$ in RCN, followed by the cycloaddition of a nitrile oxide. Despite the similarity of routes **A** and **B**, the obvious advantage of the first method is that it allows the synthesis of complexes **1**–**8** starting directly from $PdCl_2$ and omitting the unnecessary step of the isolation of *trans*-$[PdCl_2(RCN)_2]$.

In order to get a rough estimate of the effect of the Pd^{II} center on the cycloaddition rate, the reaction between $PdCl_2$ (1 equiv.) in EtCN (3 mL) and **I** or **II** (2 equiv.) at 40 °C was compared with the reaction of **I** or **II** and EtCN under the same experimental conditions; only an approximate 1.5-fold acceleration in the metal-mediated vs. metal-free synthesis was observed. It appears that Pd^{II} acts mostly as a trapping center, thus allowing a facile isolation and characterization of 1,2,4-oxadiazoles as metal-bound species.

Binding of the Nitrile Oxides by a Pd^{II} Center

The interaction between $[PdCl_2(MeCN)_2]$ and the nitrile oxides **I** and **II** proceeds in another direction when dichloromethane is used as solvent instead of MeCN: the reaction gives (nitrile oxide)palladium(II) complexes **9** and **10** (Scheme 1, route **C**). In the electrospray mass spectra of both complexes, we observed the $[M + H]^+$ ion with the expected isotopic pattern. Complex **10** gave satisfactory C, H, and N microanalyses, whereas we failed to get reproducible data for the rather unstable **9**. In the IR spectra of both complexes, strong (**9**) or medium (**10**) bands of $\nu(C{\equiv}N)$ are shifted toward lower frequencies (15 cm^{-1} for **9** and 56 cm^{-1} for **10**) upon coordination. The ^1H NMR spectra display all required resonances with their expected integration. In $CDCl_3$, the complexes exist as a number of conformers probably because of the hindered rotation of the bulky ligands.

Although, to the best of our knowledge, metal complexes with nitrile oxides as ligands are unknown, there are a few reports of 1,3-dipolar cycloadditions where the formation of complexes between Lewis acids and nitrile oxides was assumed, from indirect evidence, to occur.[25,26] The major argument supporting the idea of the formation of (nitrile oxide)[M] complexes is based on the inhibition of the 1,3-

dipolar cycloaddition (sometimes with an increase of selectivity of the reaction[25–29]) in the presence of metal centers, which, in agreement with the authors,[25,26,30] blocks the oxygen atom of the nitrile oxide by coordination. The latter hypothesis was supported in the framework of this study by the lack of formation of (oxadiazole)palladium(II) complexes when **9** or **10** were treated with the corresponding nitriles (route **D**, Scheme 1).

Characterization of the (1,2,4-Oxadiazole)palladium(II) Complexes

Complexes **1**–**8** were characterized by C, H, and N analyses. In their FAB spectra they display the quasi-ion $[M + Na]^+$ (**1**, **2**) and/or the fragmentation $[M - H]^+$ and/or $[M - Cl]^+$ ions (**1**, **2**, **5**, **7**, and **8**); for **3**, **4**, and **6** only deep fragmentation was observed. In their IR spectra, the oxadiazole complexes **1**–**8** exhibit two relatively strong bands in the range of 1537–1658 cm^{-1}. The first one lies in a relatively narrow interval, i.e. 1607–1614 cm^{-1}, for all these complexes, and can be attributed to a ν(C=N) stretching vibration in the oxadiazole ligand. The position of the second band varies and depends on the type of the complex. Thus, medium-to-strong and strong bands at 1537–1585 cm^{-1} (**1**, **2**, **4** derived from **I**) and 1598 cm^{-1} (**6** and **7** derived from **II**) can be attributed to the other ν(C=N) stretching vibration of the heterocycle and/or ν(C=C) stretch of the aromatic ring. In contrast to the alkyl and aryl derivatives of oxadiazoles, the dialkylcyanamide ones (**4** and **8**) do not display strong peaks in the area 1537–1585 cm^{-1} but exhibit a strong band in the range 1657–1658 cm^{-1}. This shift is probably the consequence of a different electron distribution in the dialkylcyanamide-substituted oxadiazole ligands (see below).

In the ^{1}H and ^{13}C{^{1}H} NMR spectra of [PdCl$_2$(1,2,4-oxadiazole)$_2$], two (**1**–**4** and **6**–**8**) or five (**5**) sets of each signal (or a group of signals) were detected; this is probably due to the hindered rotation of the bulky oxadiazole ligands around the Pd–N bond, which leads to inequivalence of the protons and carbon atoms. In the ^{13}C{^{1}H} NMR spectra, two carbons from the N=C–N and N=C–O moieties were detected at δ = 164–171 and 178–190 ppm, respectively. These assignments are based upon the data for similar platinum(IV) and platinum(II) oxadiazole complexes, i.e. $[PtCl_4\{N^a{=}C(R)ON{=}C^bC_6H_2R'_3)(N^a\text{–}C^b)\}_2]$ and $[PtCl_2\{N^a{=}C(R)ON{=}C^bC_6H_2R'_3)(N^a\text{–}C^b)\}_2]$, where the signals of C from the N*C*N and N*C*O groups can be distinguished by using the long-range selective INEPT technique. In the ^{1}H NMR spectra of both **4** and **8**, the signal from Me in NMe$_2$ is broad, apparently because of the hindered rotation of the NMe$_2$ group (see later).

Crystal Structure Determinations of (1,2,4-Oxadiazole) palladium(II) Complexes

Crystals of **2** (Figure 1), **3** (Figure 2), **7** (Figure 3), and **8** (Figure 4) were obtained directly from the reaction mixtures and their structures were determined by X-ray crystallography.

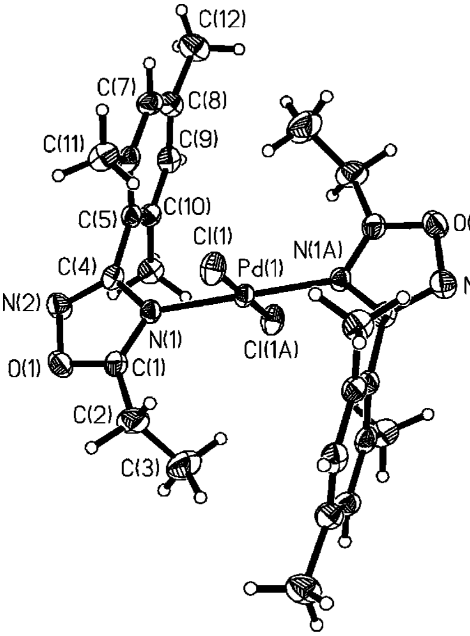


Figure 1. Thermal ellipsoid view of $[PdCl_2\{N^a{=}C(Et)ONC^b(C_6H_2Me_3)(N^a\text{–}C^b)\}_2]$ (**2**)with atomic numbering scheme; thermal ellipsoids are drawn with 50% probability

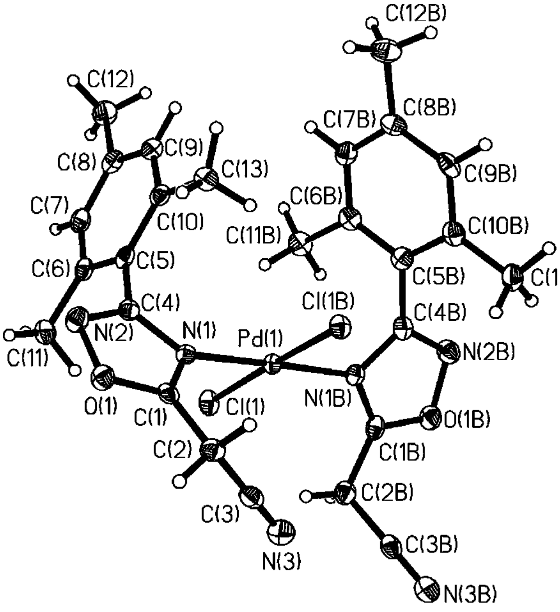


Figure 2. Thermal ellipsoid view of $[PdCl_2\{N^a{=}C(CH_2CN)ONC^b(C_6H_2Me_3)(N^a\text{–}C^b)\}_2]$ (**3**)with atomic numbering scheme; thermal ellipsoids are drawn with 50% probability

The 1,2,4-oxadiazole ligands in all these complexes are coordinated in mutual *trans* positions. In **2**, **7**, and **8** the heterocycles have an antiparallel orientation [angles between N(1)–C(1)–O(1)–N(2)–C(4) planes are 0°, 57.63(9)°, 10.16(14)°, and 0° for **2**, **3**, **7**, and **8**, respectively], while in **3**, they are turned in one direction and the torsion angle is approximately 60°. The geometrical parameters of the heterocycles in **2**, **3**, and **7** are the same within 3σ and are

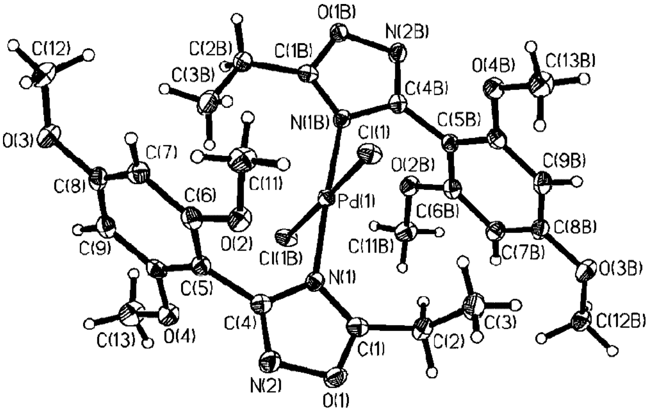


Figure 3. Thermal ellipsoid view of [PdCl$_2${N^a=C(Et)ONC^b(C$_6$H$_2$(OMe)$_3$(N^a–C^b)}$_2$] (**7**) with atomic numbering scheme; thermal ellipsoids are drawn with 50% probability

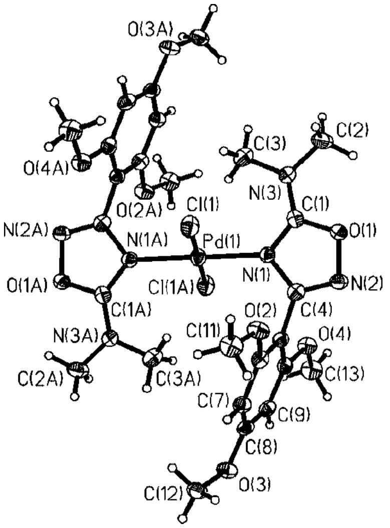


Figure 4. Thermal ellipsoid view of [PdCl$_2${N^a=C(NMe$_2$)ONC^b(C$_6$H$_2$(OMe)$_3$)(N^a–C^b)}$_2$] (**8**)with atomic numbering scheme; thermal ellipsoids are drawn with 50% probability

similar to those in the previously described (1,2,4-oxadiazole)platinum(IV) and -platinum(II) complexes,[19] in 1,2,4-oxadiazole complexes of other metals,[31] and even in the uncomplexed heterocycles.[32–34] The Pd–N and Pd–Cl bond lengths and angles around the Pd center are similar to those given in the literature for [PdCl$_2$(N-coordinated heterocycle)$_2$]-type complexes.[35]

The C=N bond length in the Pd–N=C–N fragment of **8** [1.377(5) Å] is larger than that for the corresponding bond in **2**, **3**, and **7** [1.306(3)–1.314(3) Å] and also larger than those in the free oxadiazoles bearing NRR′ substituents.[36] In addition, the C(1)–N(3) bond length in the *C*NMe$_2$ fragment [1.315(5) Å] is shorter than a normal C–N single bond and even shorter than the C=N bond in the oxadiazole ring; all these facts favor a significant double-bond character in the *C*NMe$_2$ moiety. A possible rationale for the latter observation is the dominance of the right-hand structure (Figure 5) in the mesomeric hybrid of the heterocycle.

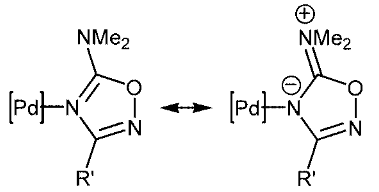


Figure 5. Possible mesomeric forms of the heterocycle in complex **8**

This observation is coherent with the unusual IR data (strong band at 1658 cm^{-1}, see above) and NMR spectroscopic data in solution, where the NMe$_2$ signal is broad probably due to hindered rotation around the partially double CN bond of the CNMe$_2$ functionality.

Liberation of the 1,2,4-Oxadiazoles

Although the activation of nitriles by Pd^{II} toward the cycloaddition is not advantageous from synthetic viewpoint, we still developed a method for liberation of 1,2,4-oxadiazoles from their complexes with the hope of further progress in this area which can be associated with either the application of cationic Pd^{II} complexes or the use of supporting ligands with pronounced π-acceptor properties.[20]

Complexes **1**–**8** are stable and remain intact in an excess of nitrile even at 40 °C for 24 h, thus preventing the reaction from being catalytic. However, the liberation of the oxadiazoles from **1**–**8** was successfully performed by substitution following two routes. In the first one, a solution of **1**–**8** in CDCl$_3$ was treated with two equivalents of 1,2-bis(diphenylphosphanyl)ethane (dppe) and, after 3 h, when the precipitation of the colorless complex [Pd(dppe)$_2$]Cl$_2$ [^{31}P{^{1}H} (CDCl$_3$): δ = 53.15 ppm (ref.[37] δ = 56.7 ppm)] was complete, the quantitative formation of the free oxadiazoles **11**–**18** was confirmed by ^{1}H NMR spectroscopy. In the preparative experiment, the precipitate of [Pd(dppe)$_2$]Cl$_2$ can easily be separated by filtration, and subsequent evaporation of the filtrate gives the 1,2,4,-oxadiazoles in the almost quantitative yield.

In the second route, a solution of **1**–**8** in CH$_2$Cl$_2$ was treated with an excess of Na$_2$S·7H$_2$O in MeOH to immediately give a precipitate of PdS; the free oxadiazoles **11**–**18** remain in solution. After separation of PdS by filtration, the solvent was evaporated from the filtrate and the 1,2,4-oxadiazoles were extracted almost quantitatively from the residue with CH$_2$Cl$_2$. The second method is preferable because Na$_2$S is much cheaper than dppe and the formation of PdS proceeds substantially faster than that of [Pd(dppe)$_2$]Cl$_2$.

The liberated 1,2,4-oxadiazoles (**11**–**18**) were characterized by positive-ion FAB mass spectrometry – typically the [M + H]$^+$ ion is observed – and ^{1}H and ^{13}C{^{1}H} NMR spectroscopy. The chemical shifts in the ^{1}H and ^{13}C{^{1}H} NMR spectra of **11**–**18** are similar to those for the corresponding (1,2,4-oxadiazole)palladium(II) complexes. However, for **11**–**14** and **16**–**18** each proton or carbon has one set of signals, in contrast to the situation described previously for the Pd complexes, i.e. the NMR inequivalence of the oxadiazoles **11**–**14** and **16**–**18** disappears when they are liberated from the corresponding palladium(II) complexes. However, in the case of **15**, five sets of signals are still displayed in the spectra for each proton and carbon atom (in the temperature range from 20 to 50 °C) and we believe that this is due to different conformations of the oxadiazole **15** bearing the two bulky substituents in the ring (Ph and $C_6H_2Me_3$). For all free oxadiazoles **11**–**18**, the N=C–N and N=C–O carbons lie in the ranges δ = 164–168 and 168–180 ppm, respectively.

Final Remarks

The results from this work can be considered from at least two perspectives. From the first one, the developed method, which is based on [2 + 3] cycloaddition of nitriles and nitrile oxides in the presence of a trapping metal center, is an excellent entry to 1,2,4-oxadiazole–metal complexes, whose chemistry is almost unknown, although the opposite holds true for metal compounds of the isomeric 1,3,4-oxadiazole; the latter complexes exhibit a good number of useful properties. From the second perspective, we have found the first example of nitrile oxide–metal complexes and further development of chemistry of this species may shed light on the mechanisms of the still poorly understood metal-mediated 1,3-dipolar cycloaddition of propargyl/allenyl anion type dipoles to nitriles.[19,38] We observed that the more labile Pd^{II} center (as compared to a kinetically inert Pt^{IV} center) reacts to a similar degree with both the dipolarophile and the dipole, and the latter interaction, i.e. ligation of nitrile oxide observed in this work for the first time, inhibits the 1,3-dipolar cycloaddition by blocking the oxygen center of the dipole. The latter points to the need for the selective complexation of metal centers with nitrile dipolarophiles (rather than with nitrile oxide dipoles) to promote the cycloaddition.

Experimental Section

Materials and Instrumentation: Solvents were obtained from commercial sources and used as received. The complexes $[PdCl_2\text{-}(RCN)_2]$ (R = Me, Et, Ph[24]) and the nitrile oxides 2,4,6-$Me_3C_6H_2CNO$ and 2,4,6-$(MeO)_3C_6H_2CNO$[23] were prepared as described previously. C,H,N elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. Positive-ion FAB mass spectra were obtained on a Trio 2000 instrument by bombarding 3-nitrobenzyl alcohol (NBA) matrices of the samples with 8 keV (ca. 1.28×10^{15} J) Xe atoms. Mass calibration for data system acquisition was achieved using CsI. Infrared spectra (4000–400 cm^{-1}) were recorded with a JASCO FT/IR-430 instrument in KBr pellets. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ spectra in $CDCl_3$ were measured with a Varian UNITY 300 spectrometer at ambient temperature.

Cycloaddition of Nitrile Oxides to Pd-Bound Nitriles. Method A: $PdCl_2$ (12 mg, 0.068 mmol, 1 equiv.) and 3–4 equiv. of **I** (32–44 mg, 0.200–0.271 mmol) or **II** (42–56 mg, 0.200–0.271 mmol) were suspended in RCN (R = Me, Et, Ph, NMe_2; 0.3 mL) or in a solution of $NCCH_2CN$ (27 mg, 0.408 mmol) in CH_2Cl_2 (3 mL) and the mixture was heated to 40 °C for 12–18 h. During this period the $PdCl_2$ dissolved to give orange (for **I**) or dark-brown (for **II**) solutions. In the case of complexes **1**–**3** and **6**–**8**, orange crystals were formed at the top of the vial and were removed by filtration (yields are 20–40%). The orange solution (reaction with **I**,complexes **4** and **5**) was evaporated to dryness under vacuum and the orange oil formed was crystallized under a layer of Et_2O to furnish an additional amount (yields are 30–50%) of the cycloaddition product (for **1**–**3**). All oxadiazole complexes (**6**–**8**) derived from **II** were crystallized from the reaction mixture and separated by filtration. The dark reaction mixture formed in the case of nitrile oxide **II** and PhCN and $PhCH_2CN$ contains a number of products and was not further investigated.

Method B: $[PdCl_2(RCN)_2]$ (R = Me, Et, Ph; 15 mg) was suspended with 3–4 equiv. of the nitrile oxides in the corresponding nitrile RCN (R = Me, Et, Ph; 0.3 mL), and the reaction mixture was heated to 40 °C for 12–18 h, whereupon an orange product formed. The isolation procedures are similar to those described above. This method was applied for the preparation of **1**, **2**, and **5**–**7**.

$[PdCl_2\{N^a{=}C(Me)ONC^b(C_6H_2Me_3)(N^a–C^b)\}_2]$ (1): Yield: 32 mg (80–85%). $C_{24}H_{28}Cl_2N_4O_2Pd$ (581.8): calcd. C 49.54, H 4.85, N 9.63; found C 49.95, H 5.15, N 9.68. FAB^+-MS: *m*/*z* = 605 $[M + Na]^+$, 581 $[M - H]^+$, 547 $[M - Cl]^+$, 508 $[M - 2HCl]^+$. IR (KBr, selected bands): 2976 (w) and 2925 cm^{-1} (w) ν(C–H), 1610 (mw) and 1585 (m) ν(C=N) and ν(C=C). ^1H NMR (300 MHz, $CDCl_3$; two sets of signals in the approximate ratio3:2): δ = 2.00 (major) and 2.29 (minor) (s, 6 H, *o*-$CH_3C_6H_2$), 2.40 (minor) and 2.51 (major) (s, 3 H, *p*-$CH_3C_6H_2$), 2.90 (minor) and 3.26 (major) (s, 3 H, $N{=}CCH_3$), 6.93 (major) and 7.04 (minor) (s, 2 H, *m*-Ar) ppm. $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$; two sets of signals): δ = 14.00 (minor) and 14.6 (major) ($N{=}CCH_3$), 20.4 (major) and 20.8 (minor) (*o*-$CH_3C_6H_2$), 21.4 (minor) and 21.5 (major) (*p*-$CH_3C_6H_2$), 120.3 (major) (C_{ipso}), 128.4 (minor) and 128.5 (major) (*m*-Ar), 138.8 (major) and 139.0 (minor) (*o*-Ar), 140.4 (major) and 141.2 (minor) (*p*-Ar), 166.6 (two N=C–N), 178.0 (Pd–N=C–O) ppm.

$[PdCl_2\{N^a{=}C(Et)ONC^bC_6H_2Me_3)(N^a–C^b)\}_2]$ (2): Yield: 32 mg (70–80%). $C_{26}H_{32}Cl_2N_4O_2Pd$ (609.9): calcd. C 51.20, H 5.29, N 9.19; found C 51.42, H 5.50, N 9.11. FAB^+-MS: *m*/*z* = 633 $[M + Na]^+$, 575 $[M - Cl]^+$, 537 $[M–Cl–HCl]^+$. IR (KBr, selected bands): 2982 (w) and 2921 cm^{-1} (w) ν(C–H), 1611 (mw) and 1573 (m) ν(C=N) and ν(C=C). ^1H NMR (300 MHz, $CDCl_3$; two sets of signals in the approximate ratio 1:1): δ = 1.46 and 1.72 (t, *J* = 7.5 Hz, 3 H, CH_2CH_3), 1.99 and 2.28 (s, 6 H, *o*-$CH_3C_6H_2$), 2.40 and 2.51 (s, 3 H, *p*-$CH_3C_6H_2$), 3.25 and 3.71 (q, *J* = 7.5 Hz, 2 H, CH_2CH_3), 6.93 and 7.04 (s, 2 H, *m*-Ar) ppm. $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$; two sets of signals): δ = 10.25 and 10.30 (CH_2CH_3), 20.5 and 20.9 (*o*-$CH_3C_6H_2$), 21.4 and 21.5 (*p*-$CH_3C_6H_2$), 21.7 and 22.4 (CH_2CH_3), 120.6 and 121.2 (C_{ipso}), 128.4 and 128.6 (*m*-Ar), 138.9 and 139.2 (*o*-Ar), 141.1 and 140.4 (*p*-Ar), 166.4 and 166.6 (N=C–N), 181.4 (Pd–N=C–O) ppm.

$[PdCl_2\{N^a{=}C(CH_2CN)ONC^bC_6H_2Me_3)(N^a–C^b)\}_2]$ (3): Yield: 17 mg (40%). $C_{26}H_{26}Cl_2N_6O_2Pd\cdot0.25CH_2Cl_2$ (631.9): calcd. C 48.28, H 4.10, N 12.87; found C 48.68, H 4.26, N 12.82. In our FAB experimental conditions, we were able to observe only deep fragmentation and no $[M]^+$ was found. IR (KBr, selected bands): 2966 (mw) and 2909 cm^{-1} (mw) ν(C–H), 2266 (vw)ν(C≡N), 1610 (mw) and 1585 (m) ν(C=N) and ν(C=C). ^1H NMR (300 MHz, $CDCl_3$; two sets of signals in the approximate ratio 1:6): δ = 1.98 (major) and 2.20 (minor) (s, 6 H, *o*-$CH_3C_6H_2$), 2.34 (minor) and 2.52 (major) (s, 3 H, *p*-$CH_3C_6H_2$), 3.61 (minor) and 4.89 (major) (s, 2 H, CH_2CN), 6.96 (minor) and 6.99 (major) (s, 2 H, *m*-Ar) ppm. $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ = 19.3 (CH_2), 20.4 (*o*-

$CH_3C_6H_2$), 21.5 (p-$CH_3C_6H_2$), 111.4 (C≡N), 128.8 (m-Ar), 139.0 (o-Ar), 141.3 (p-Ar), 171.4 (N=C–N), 190.5 (Pd–N=C–O) ppm; C_{ipso} was not detected.

$[PdCl_2\{N^a{=}C(NMe_2)ONC^bC_6H_2Me_3)(N^a–C^b)\}_2]$ (4): Yield: 17 mg (40%). $C_{26}H_{34}Cl_2N_6O_2Pd$ (639.9): calcd. C 48.89, H 5.37, N 13.17; found C 48.84, H 5.44, N 12.94. In our FAB experimental conditions, we were able to observe only deep fragmentation and no[M]$^+$ was found. IR (KBr, selected bands): 2923 cm^{-1}) (mw) ν(C–H), 1658 (ms) and 1609 (m) ν(C=N) and ν(C=C). ^{1}H NMR (300 MHz, $CDCl_3$; two sets of signals in the approximate ratio 1:2): δ = 2.29 (s, 3 H, p-$CH_3C_6H_2$, minor), 2.33 (s, 6 H, o-$CH_3C_6H_2$, major), 2.39 (s, 3 H, p-$CH_3C_6H_2$, major), 3.39 (br. s, 6 H, NMe_2), 6.88 (s, 2 H, m-Ar, minor), 6.98 (s, 2 H, m-Ar, major) ppm. $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ = 20.8 (o-$CH_3C_6H_2$), 21.3 (p-$CH_3C_6H_2$), 40.1 (NMe_2), 128.2 (m-Ar), 139.6 (o-Ar), 140.4 (p-Ar), 166.9 (N=C–N) ppm; signals of other groups were not detected.

$[PdCl_2\{N^a{=}C(Ph)ONC^bC_6H_2Me_3)(N^a–C^b)\}_2]$ (5): Yield: 19 mg (40%). $C_{34}H_{32}Cl_2N_4O_2Pd$ (706.0): calcd. C 57.84, H 4.57, N 7.94; found C 57.37, H 4.38, N 7.68. FAB$^+$-MS: m/z = 668 [M – HCl]$^+$, 633 [M – 2Cl]$^+$. IR (KBr, selected bands): 2918 cm^{-1} (mw) ν(C–H), 1607 (m) and 1557 (ms) ν(C=N) and ν(C=C). ^{1}H NMR (300 MHz, $CDCl_3$; five sets for each signal in the spectrum): δ = 2.05–2.55 (several s, 9 H, o- and p-$CH_3C_6H_2$), 6.92–7.09 (several s, 2 H, m-Ar), 7.48–7.72 (several m, 3 H, m- and p-Ph from PhC=N), 8.20–9.28 (several d, 2 H, o-Ph from PhC=N) ppm. $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ = 20.4, 20.6, 20.8, 20.9, 21.5 and 21.6 (o- and p-$CH_3C_6H_2$), 128.5–129.3, 129.9–130.6, 132.1–134.5 and 138.3–140.9 (Ph and C_6H_2), 167.5 (C=N) ppm.

$[PdCl_2\{N^a{=}C(Me)ONC^b(C_6H_2(OMe)_3)(N^a–C^b)\}_2]$ (6): Yield: 23 mg (50%). $C_{24}H_{28}Cl_2N_4O_8Pd$ (677.8): calcd. C 42.53, H 4.16, N 8.27; found C 42.00, H 4.27, N 8.10. In our FAB experimental conditions, we were able to observe only deep fragmentation and no [M]$^+$ was found. IR (KBr, selected bands): 2942 cm^{-1} (mw) and 2842 (w) ν(C–H), 1614 (s) and 1598 (s) ν(C=N) and ν(C=C). ^{1}H NMR (300 MHz, $CDCl_3$; two sets of signals in the approximate ratio 2:1): δ = 2.90 (major) and 3.27 (minor) (s, 3 H, Me), 3.57 (minor) and 3.83 (major) (s, 6 H, o-$CH_3C_6H_2$), 3.91 (major) and 3.98 (minor) (s, 3 H, p-$CH_3OC_6H_2$), 6.14 (minor) and 6.25 (major) (s, 2 H, m-Ar) ppm. $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ = 13.9 (Me), 55.8 (o-$CH_3OC_6H_2$), 56.0 (p-$CH_3OC_6H_2$), 90.3 (m-Ar), 160.7 (o-Ar) ppm.

$[PdCl_2\{N^a{=}C(Et)ONC^b(C_6H_2(OMe)_3)(N^a–C^b)\}_2]$ (7): Yield: 24 mg (50%). $C_{26}H_{32}Cl_2N_4O_8Pd$ (705.9): calcd. C 44.24, H 4.57, N 7.94; found C 43.77, H 4.78, N 7.72. FAB$^+$-MS: m/z = 671 [M – Cl]$^+$. IR (KBr, selected bands): 2941 cm^{-1} (mw) and 2845 (w) ν(C–H), 1614 (s) and 1589 (ms) ν(C=N) and ν(C=C). ^{1}H NMR (300 MHz, $CDCl_3$; two sets of signals in the approximate ratio 3:1): δ = 1.50 (major) and 1.68 (minor) (t, J = 7.5 Hz, 3 H, Et), 3.29 (major) and 3.80 (minor) (q, J = 7.5 Hz, 2 H, Et), 3.57 (minor) and 3.81 (major) (s, 6 H, o-$CH_3C_6H_2$), 3.91 (major) and 3.99 (minor) (s, 3 H, p-$CH_3OC_6H_2$), 6.14 (minor) and 6.25 (major) (s, 2 H, m-Ar) ppm. $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ = 10.2 (CH_3 from Et), 21.7 (CH_2 from Et), 55.7 (o-$CH_3OC_6H_2$), 55.9 (p-$CH_3OC_6H_2$), 90.2 (m-Ar), 160.7 (o-Ar), 162.7 (p-Ar), 164.5 (N=C–N), 180.3 (Pd–N=C–O) ppm.

$[PdCl_2\{N^a{=}C(NMe_2)ONC^b(C_6H_2(OMe)_3)(N^a–C^b)\}_2]$ (8): Yield: 20 mg (40%). $C_{24}H_{28}Cl_2N_4O_8Pd$ (735.9): calcd. C 42.43, H 4.66, N 11.42; found C 42.90, H 4.93, N 11.34. FAB$^+$-MS: m/z = 700 [M – Cl –H]$^+$. IR (KBr, selected bands): 2935 cm^{-1} (mw) and 2845 (w) ν(C–H), 1657 (s) and 1614 (s) ν(C=N) and ν(C=C). ^{1}H NMR (300 MHz, $CDCl_3$; two sets of signals in the approximate ratio 11:1; signal sets for minor isomer are not given because of its low abundance): δ = 3.45 (br. s, 3 H, Me), 3.78 (s, 6 H, o-$CH_3C_6H_2$), 3.92 (s, 3 H, p-$CH_3OC_6H_2$), 6.19 (s, 2 H, m-Ar) ppm. $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ = 39.4 (NMe_2), 55.7 (o-$CH_3OC_6H_2$), 56.1 (p-$CH_3OC_6H_2$), 90.1 (m-Ar) ppm; signals for other groups were not detected due to poor solubility of compound.

(Nitrile oxide)palladium(II) Complexes: $[PdCl_2(MeCN)_2]$ (20 mg, 0.08 mmol) and the nitrile oxides R′CNO [0.20 mmol; R′ = $Me_3C_6H_2$**I**, $(MeO)_3C_6H_2$**II**] were suspended in CH_2Cl_2 (3 mL) and the mixture left to stand at room temperature for 2–4 h. During this period the $[PdCl_2(MeCN)_2]$ dissolved to give dark-brown solutions. In case of **II** the brown solution remained unchanged after several hours, therefore the solvent was evaporated and the dark oily residue formed was crystallized under a layer of Et_2O. In the case of **I**, after several hours an orange precipitate begin to form and solution become more pale and turned to orange-yellow. The precipitate was removed by decantation and the solution was evaporated under vacuum until dryness and crystallized under a layer of Et_2O. Yield: ca. 60% (**9**) and ca. 30% (**10**).

$[PdCl_2(ONCC_6H_2Me_3)_2]$ (9): ES-MS$^+$: m/z = 501 [M + H]$^+$. IR (KBr, selected bands): 2967 cm^{-1} (w) and 2922 (mw) ν(C–H), 2278 (s) ν(C≡N) 1792 (ms), 1735 (m), 1608 (s), 1456 (br. ms) [in the free nitrile oxide: 2949 (w) and 2919 (mw) ν(C–H), 2293 (s) ν(C≡N), 1608 (m)]. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.30–2.49 (set of s, 9 H, o- and p-$CH_3C_6H_2$), 6.89–6.94 (set of s, 2 H, C_6H_2) ppm.

$[PdCl_2\{ONCC_6H_2(OMe)_3\}_2]$ (10): $C_{20}H_{22}Cl_2N_2O_8Pd$ (595.9): calcd. C 40.32, H 3.72, N 4.70; found C 40.90, H 4.64, N 4.63. ES-MS$^+$: m/z = 597 [M + H]$^+$. IR (KBr, selected bands): 2940 cm^{-1} (mw) ν(C–H), 2249 (m) ν(C≡N) 1606 (br. s), 1456 (br. m) [in the free nitrile oxide: 2985 (w) and 2949 (mw) ν(C–H), 2305 (ms) ν(C≡N), 1608 (s), 1582 (s), 1469 (ms)]. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.76–3.94 (set of s, 9 H, o- and p-$CH_3OC_6H_2$), 6.02–6.14 (set of s, 2 H, C_6H_2) ppm.

Liberation of the Oxadiazoles from Complexes 1–8: (*i*) dppe (2 equiv.) was added to a solution of **1**–**8** (15 mg) in $CDCl_3$ (0.5 mL) and the mixture was allowed to stand at 40 °C for 30 min, whereupon colorless $[Pd(dppe)_2]Cl_2$ precipitated. The free oxadiazole was characterized in solution by ^{1}H NMR spectroscopy. Evaporation of the solvent gave **11**–**18** (see later) in almost quantitative yield.(*ii*) A solution of $Na_2S{\cdot}7H_2O$ (50 mg) in MeOH (1 mL) was added dropwise to a solution of **1**–**8** (10 mg) in CH_2Cl_2 (0.5 mL). The dark-brown PdS precipitated immediately after the addition of ca. 0.15 mL of the sulfide solution (until the yellow color disappeared), whereupon the reaction mixture was evaporated to dryness and the oxadiazole was extracted from the residue with CH_2Cl_2 (1 mL). Yields are almost quantitative.

The oxadiazoles $N^a{=}C(Et)ONC^b(C_6H_2Me_3)(N^a–C^b)$ (**12**), and $N^a{=}C(Et)ONC^b(C_6H_2(OMe)_3)(N^a–C^b)$ (**17**) have been characterized previously.[10]

$N^a{=}C(Me)ONC^b(C_6H_2Me_3)(N^a–C^b)$ (11): FAB$^+$-MS: m/z = 203 [M + H]$^+$. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.18 (s, 6 H, o-$CH_3C_6H_2$), 2.33 (s, 3 H, p-$CH_3C_6H_2$), 2.68 (s, 3 H, Me), 6.94 (s, 2 H, m-Ar) ppm. $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ = 12.4 (N=CMe), 20.0 (o-$CH_3C_6H_2$), 21.2 (p-$CH_3C_6H_2$), 128.5 (m-Ar), 137.7 (o-Ar), 139.6 (p-Ar) ppm.

$N^a{=}C(CH_2CN)ONC^b(C_6H_2Me_3)(N^a–C^b)$ (13): FAB$^+$-MS: m/z = 228 [M + H]$^+$. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.20 (s, 6 H, o-$CH_3C_6H_2$), 2.34 (s, 3 H, p-$CH_3C_6H_2$), 4.19 (s, 2 H, CH_2), 6.96 (s, 2 H, m-Ar) ppm. $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ = 17.3 (Me), 20.2 (o-$CH_3C_6H_2$), 21.2 (p-$CH_3C_6H_2$), 112.0 (C≡N), 122.6 (C_{ipso}), 128.7 (m-Ar), 137.8 (o-Ar), 140.3 (p-Ar), 168.1 (N=C–O), 169.1 (N=C–N) ppm.

Table 1. Crystal data for compounds **2**, **3**, **7**, and **8**

	2	**3**	**7**	**8**
Empirical formula	$C_{26}H_{32}Cl_2N_4O_2Pd$	$C_{26}H_{22}Cl_2N_6O_2Pd$	$C_{26}H_{32}Cl_2N_4O_8Pd$	$C_{26}H_{34}Cl_2N_6O_8Pd$
Mol. mass	609.86	627.80	705.86	735.89
Temp [K]	110(2)	100(2)	110(2)	100(2)
λ [Å]	0.71073	0.71073	0.71073	0.71073
Cryst. syst.	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P2_1/c$
a [Å]	8.03300(10)	13.5346(2)	16.3357(2)	11.1938(5)
b [Å]	6.7074(2)	16.0527(3)	7.62820(10)	8.1204(3)
c [Å]	24.7117(6)	13.7351(3)	22.8554(3)	16.5640(7)
β [°]	92.7290(10)	117.1703(8)	91.8986(4)	94.045(2)
V [Å^3]	1329.97(5)	2654.89(9)	2846.49(6)	1501.89(11)
Z	2	4	4	2
ρ_{calc} [Mg m^{-3}]	1.523	1.571	1.647	1.627
μ(Mo-K_α) [mm^{-1}]	0.929	0.936	0.896	0.854
$R1$[a] [$I \geq 2\sigma(I)$]	0.0320	0.0310	0.0282	0.0456
$wR2$[b] [$I \geq 2\sigma(I)$]	0.0733	0.0665	0.0653	0.1128

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = \{\Sigma[w(F_o{}^2 - F_c{}^2)^2]/\Sigma[w(F_o{}^2)^2]\}^{1/2}$.

Table 2. Selected bond lengths [Å] and angles [°] for **2**, **3**, **7**, and **8**

	2	**3**	**3b**	**7**	**7b**	**8**
Ru(1)–Cl(1)	2.2899(8)	2.2947(6)	2.2927(6)	2.2940(6)	2.3082(6)	2.2952(10)
Ru(1)–N(1)	2.018(2)	2.018(2)	2.030(2)	2.024(2)	2.031(2)	2.045(3)
N(1)–C(1)	1.307(4)	1.307(3)	1.305(3)	1.314(3)	1.306(3)	1.337(5)
N(1)–C(4)		1.390(3)	1.394(3)	1.388(3)	1.396(3)	1.394(5)
C(1)–C(2)	1.476(4)	1.483(4)	1.484(4)	1.474(3)	1.481(3)	
C(1)–N(3)						1.315(5)
C(1)–O(1)	1.330(4)	1.319(3)	1.329(3)	1.328(3)	1.341(3)	1.341(5)
O(1)–N(2)	1.425(3)	1.433(3)	1.429(3)	1.430(3)	1.425(2)	1.441(4)
N(2)–C(4)	1.295(4)	1.304(3)	1.305(3)	1.297(3)	1.294(3)	1.287(5)
Cl(1)–Pd(1)–N(1)	91.83(7)	89.61(6)	90.23(6)	88.95(5)	90.58(5)	88.30(9)
Pd(1)–N(1)–C(1)	124.3(2)	125.3(2)	128.0(2)	126.8(2)	132.7(2)	129.9(3)
N(1)–C(1)–C(2)	128.3(3)	129.5(2)	130.2(2)	129.4(2)	132.4(2)	
N(1)–C(1)–N(3)						131.3(4)
N(1)–C(1)–O(1)	111.0(2)	112.3(2)	112.0(2)	111.0(2)	111.1(2)	110.9(3)
C(1)–O(1)–N(2)	107.6(2)	106.9(2)	107.1(2)	107.8(2)	107.6(2)	107.6(3)
O(1)–N(2)–C(4)	104.0(2)	104.0(2)	103.8(2)	103.5(2)	103.7(2)	103.3(3)
N(2)–C(4)–N(1)	112.5(2)	112.3(2)	112.5(2)	113.1(2)	113.2(2)	114.7(3)

N^a=C(NMe$_2$)ONC^b(C$_6$H$_2$Me$_3$)(*N^a*–*C^b*) (14): FAB$^+$-MS: *m*/*z* = 232 [M + H]$^+$. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 2.23 (s, 6 H, *o*-C*H*$_3$C$_6$H$_2$), 2.28 (s, 3 H, *p*-C*H*$_3$C$_6$H$_2$), 3.20 (br. s, 6 H, NMe$_2$), 6.89 (s, 2 H, *m*-Ar) ppm. ^{13}C{^{1}H} NMR (75.4 MHz, CDCl$_3$): δ = 19.9 (*o*-*C*H$_3$C$_6$H$_2$), 21.1 (*p*-*C*H$_3$C$_6$H$_2$), 40.2 (NMe$_2$), 128.2 (*m*-Ar), 137.5 (*o*-Ar), 139.1 (*p*-Ar) ppm; signals for other groups were not detected.

N^a=C(Ph)ONC^b(C$_6$H$_2$Me$_3$)(*N^a*–*C^b*) (15): FAB$^+$-MS: *m*/*z* = 278 [M + Na]$^+$, 265 [M + H]$^+$. ^{1}H NMR (300 MHz, CDCl$_3$; three sets of each signal in the approximate ratio 2:2:3): δ = 2.25, 2.30, and 2.34 (three s, 6 H, *o*-C*H*$_3$C$_6$H$_2$), 2.05, 2.49, and 2.55 (three s, 3 H, *p*-C*H*$_3$C$_6$H$_2$), 6.92, 6.98, and 7.09 (three s, 2 H, *m*-Ar), 7.4–7,6 (m, 3 H, *m*- and *p*-Ph), 8.22, 8.71, and 8.98 (three d, 2 H, *o*-Ph) ppm. ^{13}C{^{1}H} NMR (75.4 MHz, CDCl$_3$): δ = 20.1, 20.9 and 21.2 (*o*-*C*H$_3$C$_6$H$_2$), 20.6, 21.5 and 21.6 (*p*-*C*H$_3$C$_6$H$_2$), 128.2, 128.6, 128.7, 128.9, 129.1, 129.9, 130.6, 132.7, 133.7, 134.0, 137.8, 139.8 and 140.9 (all Ar) ppm; signals from other groups were not detected.

N^a=C(Me)ONC^b(C$_6$H$_2$(OMe)$_3$)(*N^a*–*C^b*) (16): FAB$^+$-MS: *m*/*z* = 251 [M + H]$^+$. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 2.18 (s, 6 H, *o*-C*H*$_3$OC$_6$H$_2$), 2.33 (s, 3 H, *p*-C*H*$_3$OC$_6$H$_2$), 2.68 (s, 3 H, Me), 6.94 (s, 2 *H*, *m*-Ar) ppm. ^{13}C{^{1}H} NMR (75.4 MHz, CDCl$_3$): δ = 12.5 (Me), 55.4 (*p*-*C*H$_3$OC$_6$H$_2$), 56.0 (*o*-*C*H$_3$OC$_6$H$_2$), 90.7 (*m*-Ar), 97.6 (C$_{ipso}$), 160.1 (*o*-Ar), 163.2 (*p*-Ar), 164.1 (N=C–N), 175.9 (N=C–O) ppm.

N^a=C(NMe$_2$)ONC^b(C$_6$H$_2$(OMe)$_3$)(*N^a*–*C^b*) (18): FAB$^+$-MS: *m*/*z* = 280 [M + H]$^+$. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 3.18 (s, 3 H, Me), 3.77 (s, 6 H, *o*-CH$_3$C$_6$H$_2$), 3.83 (s, 3 H, *p*-CH$_3$OC$_6$H$_2$), 6.15 (s, 2 H, *m*-Ar) ppm. ^{13}C{^{1}H} NMR (75.4 MHz, CDCl$_3$): δ = 40.4 (NMe$_2$), 56.0 (*o*-*C*H$_3$OC$_6$H$_2$), 55.4 (*p*-*C*H$_3$OC$_6$H$_2$), 90.7 (*m*-Ar), 160.1 (*o*-Ar), 162.9 (*p*-Ar), 164.0 (N=C–N), 171.6 (N=C–O) ppm; signals for other groups were not detected.

X-ray Crystal Structure Determinations: The crystals were immersed in perfluoropolyether, mounted in a cryo-loop and measured at 100 or 110 K. The X-ray diffraction data were collected with a Nonius KappaCCD diffractometer using Mo-K_α radiation (λ = 0.71073 Å). The Denzo-Scalepack program package[39] was used for cell refinements and data reductions. Structures were solved by direct methods using the SHELXS-97 or SIR-97 programs or by Patterson method using DIRDIF-99 with the WinGX graphical user interface.[40–43] An empirical absorption correction was applied to all data using XPREP in SHELXTL v.6.12[44] (T_{min}/T_{max}: 0.12334/0.15440, 0.31972/0.35415, 0.12648/0.15208, and 0.13741/0.17395 for **2**, **3**, **7**, and **8**, respectively). Structural refinements were carried out with SHELXL-97.[41] The asymmetric unit contained only half a molecule in **2** and **8**, whereas in **3** and **7** the asymmetric unit contained a whole molecule. All hydrogens were placed in idealized positions and constrained to ride on their parent atom. The crystallographic data are summarized in Table 1. Selected bond lengths and angles are shown in Table 2.

CCDC-243489 to -243492 (for **2**, **3**, **7**, and **8**, respectively) 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.

Acknowledgments

This work has been partially supported by the FCT (Foundation for Science and Technology, Portugal) and its POCTI program (POCTI/QUI/43415/2001 project; FEDER funded). N.A.B. expresses gratitude to the POCTI program, Portugal (grant SFRH/BPD/11448/2002) and the Center for Natural Sciences (Konkursnii Tsentr Fundamentalnogo Estestvoznaniya), Russia (grant PD03-1.3-28) and the Russian Fund for Basic Research (grant 05-03-32140a) for financial support. M.H. would like to thank the Academy of Finland for financial support. V.Y.K. is very much obliged to the Russian Fund for Basic Research for a grant (03-03-32363), POCTI program (FEDER funded; Cientista Convidado/Professor at the Instituto Superior Técnico, Portugal), the Royal Society of Chemistry for a Grant for International Authors, and the Academy of Finland for support of the cooperation with the University of Joensuu. The authors thank NATO for the Collaborative Linkage Grant PST.CLG.979289.

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Received July 3, 2004