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Pd^{II}-Promoted Single-Pot Template Transformations of Benzonitriles, Cyanoguanidine and Sodium Dicyanamide with the Formation of Symmetrical and Asymmetrical (1,3,5-Triazapentadienate)palladium(II) Complexes

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Treatment of benzonitriles 4-XC_6H_4CN (**1**) [X = H (**1a**), F (**1b**), Cl (**1c**), Br (**1d**), I (**1e**)] with an excess of 2-butanone oxime (Me)(Et)C=NOH (as a reagent and solvent) in the presence of $PdCl_2$ at 100 °C for 12 h affords the symmetrical cationic 2,4-diaryl-1,3,5-triazapentadiene (Htap) palladium(II) complexes $[Pd(Htap)_2]Cl_2$ (**2′**) [Htap = HN=C(4-XC_6H_4)NHC(4-XC_6H_4)=NH]. Recrystallization of **2′** from MeOH/$CHCl_3$ with two equivalents of *n*-propylamine gives the corresponding neutral triazapentadienate (tap) complexes $[Pd(tap)_2]$ (**2**) [tap = HN=C(4-XC_6H_4)NC(4-XC_6H_4)=NH; X = H (**2a**), F (**2b**), Cl (**2c**), Br (**2d**), I (**2e**)] in good yields. When cyanoguanidine, $HN=C(NH_2)N(H)C\equiv N$ (**3**), or sodium dicyanamide $NaN(C\equiv N)_2$ (**5**) are treated with an excess of primary alcohols, ROH [R = Me, Et, *n*Pr, *n*Bu or $(CH_2)_2OMe$] in the presence of $PdCl_2$, while being heated for 12 h, the corresponding asymmetrical 2-amino-4-alkoxy-1,3,5-triazapentadienate-Pd^{II} complexes $[Pd\{HN=C(NH_2)NC(OR)=NH\}_2]$ (**4**) [R = Me (**4a**), Et (**4b**), *n*Pr (**4c**), *n*Bu (**4d**)] or the symmetrical 2,4-dialkoxy-1,3,5-triazapentadienate-Pd^{II} complexes $[Pd\{HN=C(OR)NC(OR)=NH\}_2]$ (**6**) [R = Me (**6a**), Et (**6b**), *n*Pr (**6c**), $(CH_2)_2OMe$ (**6d**)], respectively, are formed and isolated as a mixture of isomers in good yields. All these compounds have been characterized by IR, ^1H and ^{13}C NMR spectroscopy, ESI-MS, elemental analyses and, in the case of **2c**, by XRD.

Introduction

Palladium complexes containing an imino (C=N) ligand moiety are known to be good catalysts for many organic syntheses, in particular C–C cross-coupling or carboxylation reactions.[1,2] Lately one class of such imino ligands, viz. 1,3,5-triazapentadienates N(H)=C(*R*)-N-C(R′)=N(H) (tap), has attracted increasing attention.[3–20] These compounds are triaza isoelectronic analogues of the well known and widely used *O*,*O*-β-diketonates R-C(=O)-CH-C(=O)-R, and usually coordinate to a metal ion as chelating *N*,*N*-bidentate ligands, forming stable complexes with a square planar core.[3–20] On the other hand, it was noted[9] that these ligands resemble bis(pyrazolyl)borates, another important class of ligands. Thus, tap can also potentially impact areas in which *O*,*O*-β-diketonates or bis(pyrazolyl)borates find application, such as in organic synthesis, catalysis, the preparation of optical recording materials, enzyme inhibition, analytical chemistry, etc.[21,22]

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Previously, some tap-Pd^{II} complexes were synthesized by the reaction of pre-prepared tap with metal ion sources.[3,5,6,12] These pre-prepared tap ligands usually contain N^1,N^3 nitrogen atoms connected to bulky groups, e.g. phenyls, and can be synthesized by the reaction of primary amines, RNH_2, with the fluorinated imine C_3F_7-CF=N-C_4F_9[6] or by the Ley and Muller method[23] where amidine is treated with an *N*-imidoyl chloride.[3–5,12] Another route to tap-Pd complexes involves template transformations of cyanopyridines[10,16] through lithium amidinate, which is produced in situ from $LiN(SiMe_3)_2$[10] or via an oxime-mediated process.[16] In the latter case, the synthesized complexes were shown[16] to display catalytic activity towards Suzuki–Miyaura and Heck cross-coupling reactions.

A further synthetic path to tap ligands proceeds via nucleophilic addition of alcohols to dicyanamides or cyanoguanidines that are coordinated to a metal center.[17–20] Until now only copper, nickel and platinum ions have been studied in these transformation reactions and no data on palladium(II)-mediated transformations have been reported, irrespective of the potential ability of Pd^{II} to form tap complexes[3,5,6,10,12,16] and its expected behavioural similarity to that of Pt^{II} in promoting nucleophilic addition reactions with substrates containing the C≡N group, namely organonitriles.[24–27]

Thus, one can conclude that the template conversions of C≡N-containing reagents to tap ligands bound to Pd^{II} cen-

ters deserve to be explored further as a convenient route to new tap-palladium(II) complexes. In the current study we have extended the family of triazapentadienate-palladium complexes by applying the template oxime-mediated transformation of benzonitriles, and the nucleophilic addition of alcohols to cyanoguanidine and dicyanamide.

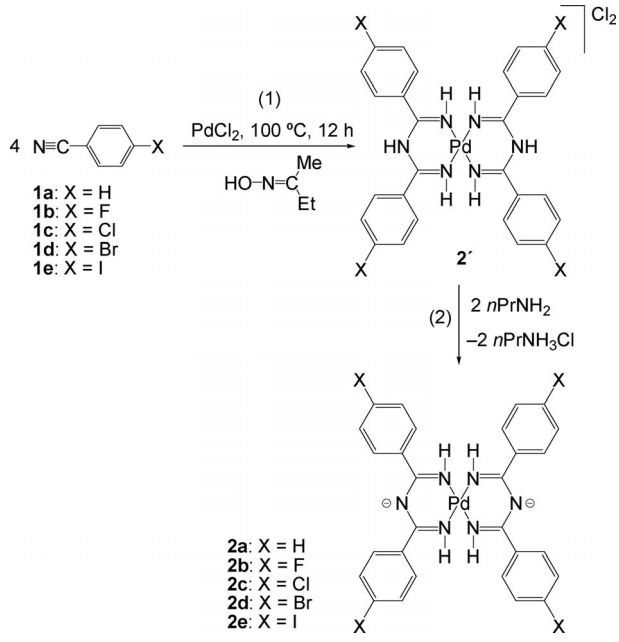
Results and Discussion

Conversion of Benzonitriles to 2,4-Diaryl-1,3,5-triazapentadienate Ligands Mediated by the Palladium(II)/2-Butanone Oxime System

Recently, we performed an easy and convenient template synthesis of tap complexes in good yields from nitriles that was mediated by oximes.[7,11,16] Initially, this procedure involved an Ni^{II} metal center, and liquid nitriles in a high excess since they acted also as solvents,[7] but a route with solid nitriles (in particular, cyanopyridine) was developed with a liquid oxime used as a solvent,[11] and the synthetic procedure was extended to involve other metal centers (in particular, Pd^{II}).[16] This route is attractive due to its simplicity and the low cost of the reagents, further it does not need special precautions and proceeds in air and in solvents and reagents that have not been predried. Thus, we have now tested a similar strategy for the synthesis of related 2,4-diaryl-1,3,5-triazapentadienate-Pd^{II} complexes.

The reactions of the unsubstituted benzonitrile 4-XC_6H_4CN (**1**) [X = H (**1a**)], and of those containing an electron-withdrawing substituent at the *para*-position [X = F (**1b**), Cl (**1c**), Br (**1d**), I (**1e**)], with palladium(II) chloride ($PdCl_2$) and 2-butanone oxime [(Me)(Et)C=NOH] for 12 h at 100 °C, lead to the formation of the cationic 1,3,5-triazapentadiene palladium(II) complexes $[Pd(Htap)_2]Cl_2$ (**2′**) that were isolated as yellow powders from the reaction mixture (Scheme 1, reaction 1), in a similar manner to the pyridine-containing nitriles we reported earlier.[16] In contrast, if acetone is used as solvent in the presence of 4 equiv. of 2-butanone oxime, only a palladium(II)-oxime complex is recovered after refluxing the reaction mixture for 1 d (see Exp. Sect.). Recrystallization of **2′** from $MeOH/CHCl_3$ with 2 equiv. of *n*-propylamine leads to the deprotonation of the central nitrogen atom in the PdN(H)=CN(*H*)-C=N(H) metallacycles to give the corresponding neutral 1,3,5-triazapentadienate compounds $[Pd\{HN{=}C(4\text{-}XC_6H_4)\text{-}NC(4\text{-}XC_6H_4){=}NH\}_2]$ (**2**) [X = H (**2a**), F (**2b**), Cl (**2c**), Br (**2d**), I (**2e**)] (Scheme 1, reaction 2). Since these complexes are more soluble in organic solvents than **2′** and more convenient for characterization, we focused our attention on their isolation and full characterization.

All complexes **2a**–**2e** were characterized by IR, ^1H and ^{13}C NMR spectroscopy, ESI-MS, elemental analyses (C, H, N) and, in the case of **2c**, by XRD. The IR spectra of **2a**–**2e** show no ν(C≡N) bands, while the characteristic ν(NH) and ν(C=N) bands are observed at ca. 3200 and ca. 1600 cm^{-1}, respectively. The ^1H and ^{13}C NMR spectra display the expected resonances at the usual chemical shifts for the expected functional groups, e.g. the phenyl rings appear in the δ = 7–8 ppm range in the ^1H NMR spectra, with the corresponding ^{13}C NMR resonances at δ = 120–140 ppm, while the *C*=N carbon atom is observed at ca. 160–170 ppm. The monoprotonated molecular ions $[M + H]^+$ are observed with the expected isotopic patterns in the ESI-MS spectra (see Exp. Sect.).



Scheme 1.

Yellow crystals of **2c** suitable for XRD analysis were obtained upon recrystallization by slow evaporation of a $MeOH/CHCl_3$ solution of **2c**, in the presence of 2 equiv. of $nPrNH_2$. In the structure of **2c** the metal cation is located on a crystallographic inversion center and two uninegatively charged *para*-chlorophenyl tap ligands act as *N,N*-bidentate chelating agents and occupy the four coordination sites of the central Pd^{II} ion, which has a slightly distorted square-planar geometry (Figure 1). The N–Pd–N bite angles [87.80(5) and 92.20(5)°] and the Pd–N bond distances [1.9783(13) and 1.9849(13) Å] are close to those observed in Pd^{II} bis-1,3,5-triazapentadienes. The negative charges on the tap ligands are delocalized over each N1C2N3C1N2 fragment that feature a delocalized π-system, which is indicated by the C(sp^2)=N character[28] of the N1–C2 and N2–C1 [1.305(2) and 1.3055(19) Å, respectively] bonds, as well as by the N3–C1 and N3–C2 distances [1.3504(19) and 1.3547(19) Å, respectively] that are characteristic of planar C(sp^2)–N(sp^2) groups.[28] The metallacycle cores are almost planar, but the Cl1- and Cl2-phenyl arms are twisted by 33.84 and 10.94°, respectively, from the core plane. Similar distortions were found in related Pd^{II} complexes.[16]

The molecules of **2c** are linked together by means of N–H–O connections with the intercalated methanol molecules (Figure 1), which operate both as H-acceptors and H-donors, and are involved in medium strong intermolecular hydrogen bonds (see legend of Figure 1). The methanol molecules are further involved in other hydrogen bond interactions, e.g. C22–H22···O10 [*d*(H···A) 2.51 Å, ∠(DH···A)

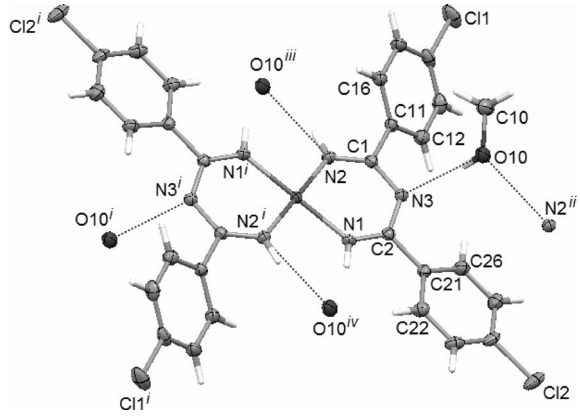


Figure 1. Crystal structure of complex **2c**, with atomic numbering scheme, showing the strongest hydrogen bonding interactions. Selected bond lengths [Å] and angles [°]: Pd1–N1 1.9849(13), Pd1–N2 1.9783(13), N1–C2 1.305(2), N2–C1 1.3055(19), N3–C1 1.3504(19), N3–C2 1.3547(19), N1–Pd1–N2 87.80(5), Pd1–N1–C2 128.14(11). Selected torsion angles [°]: N2–C1–C11–C16 37.7(2), N1–C2–C21–C22 13.4(2). Selected hydrogen bonds [*d*(H···A), ∠(DHA)]: N1–H1···O10 2.53(2) Å, 143.4(18)°, N2–H2···O10 2.14(2) Å, 162.1(18)°; O10–H10···N3 2.16(3) Å, 161(2)°. Symmetry codes: (i) 2 – *x*, 1 – *y*, –*z*; (ii) –1 + *x*, *y*, *z*; (iii) 1 + *x*, *y*, *z*; (iv) 1 – *x*, 1 – *y*, –*z*.

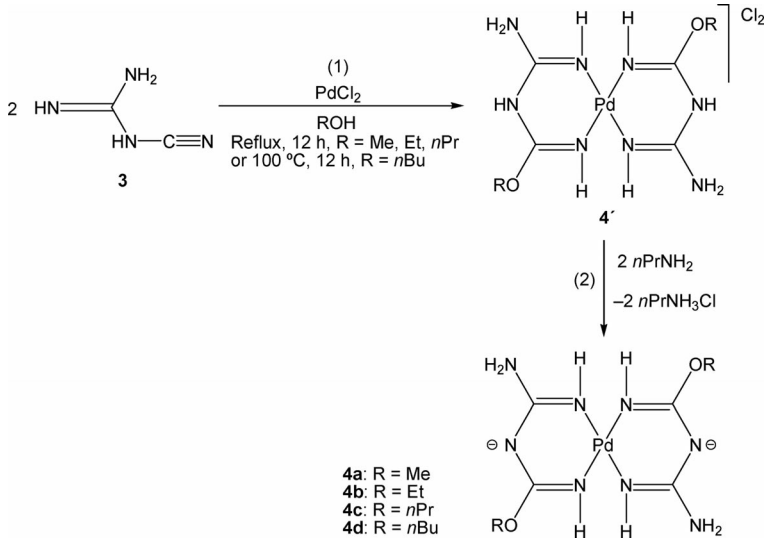
172°]. Intermolecular contacts between the chloride ions and aromatic hydrogen atoms were also detected; as a result of Cl1···H26 interactions the molecules are held together to form 1D hydrogen-bonded molecular chains, and by means of Cl2···H12 interactions the structure is extended in the second dimension (Figure S1). Furthermore, π···π stacking interactions between the C21–C26 phenyl rings and the metallacycles contribute to the formation of a supramolecular network structure (Figure S2); the centroid–centroid distances of 3.835 and 4.109 Å are within the normal range for such interactions.

The mechanism of the transformation of an aromatic nitrile into a ligated tap was not studied in detail, but we noticed that it does not proceed in the absence of the oxime or of the metal(II) salt, thus indicating that these reagents have an essential role in the process, which conceivably involves the complete hydrolysis of the nitrile to ammonia and a carboxylic acid, followed by the metal(II)-mediated reaction of the ammonia with the nitrile to yield an amidine that then couples with the cyano group of a nitrile ligand to give the tap complex.[7,11,13,16,29–33]

It is noteworthy that reactions of aliphatic liquid nitriles, such as acetonitrile or propionitrile, in excess (also playing the role of solvent) with $PdCl_2$ and 4 equiv. of acetone oxime and 2-butanone oxime were attempted, but in all cases only oxime-palladium(II) complexes of the type $[PdCl_2(oxime)_2]$ were isolated. The identity of these products was confirmed by IR, NMR and elemental analysis, and by comparison of their analytical data with those of the oxime-Pd^{II} complexes prepared independently by a known[16] modified procedure (see Exp. Sect. for details).

Conversion of Cyanoguanidine to 2-Amino-4-alkoxy-1,3,5-triazapentadienate Ligands Mediated by Palladium(II)/Primary Alcohol Systems

For the preparation of asymmetrical 2-amino-4-alkoxy-1,3,5-triazapentadienate-Pd^{II} complexes, a modified one-pot template synthesis that was reported for the methanol–cyanoguanidine integration at Pt^{II},[19] Ni^{II} and Cu^{II}[20] centers was employed. Thus, treatment of $PdCl_2$ with 2 equiv. of **3** in an aliphatic primary alcohol ROH (R = Me, Et, *n*Pr, *n*Bu) suspension, under reflux or by heating at 100 °C (in the case of *n*-butanol) for 12 h, leads to the formation of palladium(II)-1,3,5-triazapentadiene chlorides $[Pd(Htap)_2]Cl_2$ (**4′**) (Scheme 2, reaction 1). These compounds were then deprotonated by *n*-propylamine to give the corresponding Pd^{II} complexes **4a**–**4d** (Scheme 2, reaction 2). Like butanone oxime in the synthetic procedure described above, the neat alcohol plays a dual function by acting as both solvent and reactant.



Scheme 2.

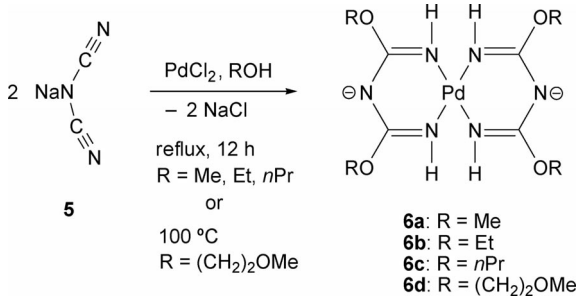
Compounds **4a**–**4d** were isolated, as pale yellow solids in good yields (73–78%), from the reaction medium by evaporation of the solvent. The reaction was successfully conducted with aliphatic linear alcohols at a temperature normally determined by the boiling point of the alcohol. In contrast, no reaction was observed when secondary alcohols such as racemic 2-butanol or *tert*-butyl alcohol were used, probably due to their bulkiness that sterically hinders the nucleophilic attack of the alcohol towards the cyano moiety in **3**. We also attempted to use **3** as a nucleophile due to its amino and imino moieties, but treatment with $PdCl_2$ (0.5 equiv.) and an excess of benzonitrile or propionitrile at 100 °C for 3 d, did not lead to the formation of any new species and only the starting materials were recovered from the reaction mixture.

Complexes **4a**–**4d** were characterized by IR, ^1H and ^{13}C NMR spectroscopy, ESI-MS and elemental analyses, which all gave data that were consistent with the proposed formulations for these compounds. The ESI-MS spectra contain $[M]^+$ or $[M + H]^+$ signals that are the most intense peaks and have characteristic isotopic distribution. The IR spectra of **4a**–**4d** show no ν(C≡N) bands and display one or two strong vibrational bands for the C=N imine moieties within the 1600–1700 cm^{-1} range, which is typical for tap-Pd^{II} complexes,[10,16] while the ν(N–H) vibrations emerge in the 3300–3400 cm^{-1} range. The ^1H and ^{13}C NMR spectra of these complexes show more than one set of signals, most probably due the presence of different isomers. For example, the ^1H NMR spectrum of complex **4a** displays three resonances at δ = 3.99, 4.01 and 4.04 ppm that are assigned to the protons of the methoxy groups (OCH_3), while the ^{13}C NMR spectrum exhibits three signals at δ = 55.2, 55.6 and 55.9 ppm for the methoxy carbon (OCH$_3$) and five signals in the δ = 152–154 ppm range related to the imino groups (*C*=NH). Possibly due to the presence of different isomeric forms, the preparation of single crystals of **4a**–**4d** suitable for XRD analysis was not successful.

Conversion of Sodium Dicyanamide to 2,4-Dialkoxy-1,3,5-triazapentadienate Ligands

The reaction of $PdCl_2$ with 2 equiv. of **5** in neat ROH (R = Me, Et, *n*Pr, $(CH_2)_2OMe$), under reflux conditions or by heating at 100 °C (in the case of 2-methoxyethanol) for 12 h, furnishes the symmetrical palladium(II) complexes **6a**–**6d** (Scheme 3). At the end of reactions the formed complex (which usually has a yellow color with an intensity that is dependent on the R substituent) is soluble in the reaction mixture, while a colorless precipitate of sodium chloride (NaCl) is formed. NaCl is partly soluble in the solvent used, but the soluble portion can be removed by evaporation of the solvent, and washing the resulting residue several times with water. The complexes **6a**–**6d** are insoluble in water, and are then recrystallized from an acetone/water (10:1) mixture to give the pure compounds.

Complexes **6a**–**6d** were characterized by IR, ^1H and ^{13}C NMR spectroscopy, ESI-MS and elemental analyses. The



Scheme 3.

ESI-MS spectra display peaks corresponding to the $[M + H]^+$ ions. The IR bands at 3331–3376 and 1608–1633 cm^{-1} prove that the N–H and C=N groups have been formed, and agree with the data for related tap-Pd^{II} complexes.[10] The ^1H and ^{13}C NMR spectra of **6a**–**6d** show, in almost all cases, more than one set of signals conceivably due the presence of different isomers in solution. For example, in the ^1H NMR spectrum of complex **6a**, the protons of the methoxy group (OCH_3) appear as a multiplet within the δ = 3.66–3.75 ppm range, while the ^{13}C NMR spectrum shows five signals in the δ = 54.9–55.7 ppm range for the methoxy carbon (OCH$_3$) and also five signals in the δ = 160.9–162.0 ppm range due to the imino group (*C*=NH). Possibly due to the presence, in solution, of complexes **6a**–**6d** in different isomeric forms, all attempts to prepare single crystals of these compounds suitable for XRD analysis failed.

Final Remarks

We synthesized, via a single-pot template transformation method, new symmetrical tap-Pd^{II} complexes **2a**–**2e** and **6a**–**6d** containing aryl and alkoxy substituents, respectively, as well as asymmetrical tap-Pd^{II} complexes **4a**–**4d** that bear amino and alkoxy substituents. The frameworks of the tap-Pd^{II} azametallacycles are conveniently provided by arenecarbonitriles (assisted by an oxime in the case of complexes **2a**–**2e**), cyanoguanidine or dicyanamide (assisted by alcohols in the cases of **4a**–**4d** and **6a**–**6d**, which also behave as the sources for the alkoxy substituents). The reactions proceed via a metal-promoted nucleophilic addition of a protic nucleophile (an oxime or an alcohol) to the cyano substrates coordinated to Pd^{II}.

The proposed syntheses are attractive due to their simplicity; they do not require special precautions and proceed in air with solvents and reagents that do not need to be predried. In a further extension to this work, an investigation into the application of the newly synthesized tap-Pd^{II} complexes as catalysts for (microwave-assisted) C–C cross-coupling reactions is currently underway in our laboratory.

Experimental Section

Materials and Instrumentation: Solvents and reagents were obtained from commercial sources (Aldrich) and used as received. C,

H and N elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. Attempts were made to measure the melting points of the compounds with a Kofler Table, but the complexes underwent decomposition upon heating (the approximate temperatures at which decomposition started are given below). ^{1}H and ^{13}C spectra (in $CDCl_3$, $CDCl_3/CD_3OD$ or [D_6]DMSO) were measured at ambient temperature on Bruker Avance II 300 and 400 MHz (UltraShield™ Magnet) spectrometers, and chemical shifts (δ) are expressed in ppm with respect to Me_4Si (^{1}H, 400.130 MHz; ^{13}C, 100.613 MHz), while J values are in Hz. Infrared spectra (4000-400 cm^{-1}) were recorded with KBr pellets on a Bio-Rad FTS 3000MX instrument 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 the 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. The compounds in methanol were continuously introduced into the mass spectrometer source with a syringe pump at a flow rate of 10 μL/min. The drying gas temperature was maintained at 350 °C and dinitrogen at 35 psi was the nebulizer gas; scanning was performed from m/z = 50 to m/z = 1500.

Reactions of Benzonitrile Derivatives 4-XC_6H_4CN 1 [X = H (1a), F (1b), Cl (1c), Br (1d), I (1e)] with $PdCl_2$ Mediated by 2-Butanone Oxime with Formation of Symmetrical (2,4-Diaryl-1,3,5-Triazapentadienate)palladium(II) Complexes 2a–2e: $PdCl_2$ (177 mg, 1.00 mmol) was stirred in 2-butanone oxime (5 mL) for 5 min, whereupon the corresponding benzonitrile derivative 4-XC_6H_4CN **1** [X = H (**1a**), F (**1b**), Cl (**1c**), Br (**1d**), I (**1e**)] (6.00 mmol) was added, and the reaction mixture was heated at 100 °C for 12 h. Homogenization of the mixture was observed within ca. 30 min, giving a yellow-brown solution. A yellow powder began to form after ca. 1 h and after 12 h the reaction mixture was filtered, and the residue washed with three 15 mL portions of acetone and dried in vacuo at room temperature to give [Pd(Htap)$_2$]Cl_2 **2′**. Recrystallization of **2′** from a hot methanol/chloroform (1:1) solution, with addition of nPrNH$_2$ (2.00 equiv. to **2′**), gave a yellow crystalline precipitate of the corresponding [Pd(tap)$_2$] (**2**) complex.

For the reactions attempted with liquid alkanenitriles, $PdCl_2$ (1.00 mmol) was stirred in acetonitrile or propionitrile (5 mL) for 5 min, whereupon acetone oxime Me_2C=NOH (case A) or 2-butanone oxime (Me)(Et)C=NOH (case B) (4.00 mmol) was added. The reaction mixture was kept under reflux by heating the solution in an oil bath for 1 d. In all the cases, the reaction mixture homogenizes after ca. 1 h after the addition of the oxime, giving a yellow solution, whereupon a yellow precipitate of [$PdCl_2$(acetone oxime)$_2$] starts to form (for case A) or the reaction mixture stays homogeneous (for case B). The yellow powder of [$PdCl_2$(acetone oxime)$_2$] (for case A) was removed from solution by filtration, washed with three 5 mL portions of acetone and dried in vacuo at room temperature. For case B, after 24 h the solvent (nitrile) was removed from the reaction mixture under vacuum, the residue was washed with three 5 mL portions of diethyl ether and dried in vacuo at room temperature. Oxime-palladium(II) complexes were recovered as the only product when acetone was the solvent and the corresponding oxime was added in a 4 equiv. amount (with 1.00 equiv. of $PdCl_2$ and 4 equiv. of benzonitrile). In this case the reaction mixture was refluxed for 1 d, whereupon the solvent was removed under vacuum. The residue was washed several times with diethyl ether to remove the starting materials and by-products. As described by us earlier,[16] palladium(II)-oxime complexes can also be prepared independently by refluxing $PdCl_2$ (2.00 mmol) with 4.00 mmol of the corresponding oxime in acetone for 12 h. Thus, the identity of the oxime-palladium(II) complexes was confirmed by IR and NMR spectroscopy, elemental analysis, and by comparison of the analytical data with those of the independently synthesized known compounds.

[Pd{HN=C(C_6H_5)NC(C_6H_5)=NH}$_2$] (2a): Yield 80% (440 mg) based on $PdCl_2$. Decomp. temp. > 250 °C. $C_{28}H_{24}N_6Pd$ (550): calcd. C 61.04, H 4.39, N 15.25; found C 61.33, H 4.22, N 15.55. ESI-MS: m/z (%) = 551 [M + H]$^+$. IR: $\tilde{\nu}$ = 3299 (NH), 1641 and 1673 (C=N) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.45–7.55 (m, 12 H, C$H_{aromatic}$), 7.83 (d, J_{HH} = 8.4 Hz, 8 H, C$H_{aromatic}$) ppm. ^{13}C{^{1}H} NMR (400 MHz, $CDCl_3$): δ = 127.3, 128.5, 132.0, 133.3 ($C_{aromatic}$), 169.4 (C=NH) ppm.

[Pd{HN=C(4-FC_6H_4)NC(4-FC_6H_4)=NH}$_2$] (2b): Yield 68% (423 mg) based on $PdCl_2$. Decomp. temp. > 280 °C. $C_{28}H_{20}F_4N_6Pd$ (622): calcd. C 53.99, H 3.24, N 13.49; found C 53.77, H 3.54, N 13.57. ESI-MS: m/z (%) = 623 [M + H]$^+$. IR: $\tilde{\nu}$ = 3179 and 3377 (NH), 1606, 1622 and 1662 (C=N) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.12–7.16 (m, 8 H, C$H_{aromatic}$), 7.84–7.87 (m, 8 H, C$H_{aromatic}$) ppm. ^{13}C{^{1}H} NMR (400 MHz, $CDCl_3$): δ = 115.7, 129.8, 163.8, 166.3 ($C_{aromatic}$), 168.4 (C=NH) ppm.

[Pd{HN=C(4-ClC_6H_4)NC(4-ClC_6H_4)=NH}$_2$] (2c): Yield 64% (440 mg) based on $PdCl_2$. Decomp. temp. > 290 °C. $C_{28}H_{20}Cl_4N_6Pd$ (688): calcd. C 48.83, H 2.93, N 12.20; found C 48.57, H 2.86, N 11.96. FAB$^+$-MS (m-NBA): m/z (%) = 689 [M + H]$^+$. IR: $\tilde{\nu}$ = 3269 (NH), 1590 (C=N) cm^{-1}. ^{1}H NMR [300 MHz, $CDCl_3$(90%), CD_3OD(10%)]: δ = 7.32 (d, J_{HH} = 8.5 Hz, 8 H, C$H_{aromatic}$), 7.87 (d, J_{HH} = 8.5 Hz, 8 H, C$H_{aromatic}$) ppm. ^{13}C{^{1}H} NMR [400 MHz, $CDCl_3$(90%), CD_3OD(10%)]: δ = 128.3, 128.6, 135.9, 137.4 ($C_{aromatic}$), 161.4 (C=NH) ppm.

[Pd{HN=C(4-BrC_6H_4)NC(4-BrC_6H_4)=NH}$_2$] (2d): Yield 65% (563 mg) based on $PdCl_2$. Decomp. temp. > 280 °C. $C_{28}H_{20}Br_4N_6Pd$ (866): calcd. C 38.81, H 2.33, N 9.70; found C 39.01, H 2.54, N 9.81. ESI-MS: m/z (%) = 867 [M + H]$^+$. IR: $\tilde{\nu}$ = 1597 and 1647 (C=N) cm^{-1}. ^{1}H NMR (300 MHz, CD_3OD): δ = 7.58 (d, J_{HH} = 8.6 Hz, 8 H, C$H_{aromatic}$), 7.65 (d, J_{HH} = 8.6 Hz, 8 H, C$H_{aromatic}$) ppm. ^{13}C{^{1}H} NMR (400 MHz, CD_3OD): δ = 129.1, 130.4, 132.4, 133.4 ($C_{aromatic}$), 169.0 (C=NH) ppm.

[Pd{HN=C(4-IC_6H_4)NC(4-IC_6H_4)=NH}$_2$] (2e): Yield 67% (706 mg) based on $PdCl_2$. Decomp. temp. > 270 °C. $C_{28}H_{20}I_4N_6Pd$ (1054): calcd. C 31.89, H 1.91, N 7.97; found C 32.11, H 2.23, N 8.05. ESI-MS: m/z (%) = 1055 [M + H]$^+$. IR: $\tilde{\nu}$ = 3179 and 3365 (NH), 1622 and 1661 (C=N) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.55 (d, J_{HH} = 8.4 Hz, 8 H, C$H_{aromatic}$), 7.82 (d, J_{HH} = 8.4 Hz, 8 H, C$H_{aromatic}$) ppm. ^{13}C{^{1}H} NMR (400 MHz, $CDCl_3$): δ = 128.9, 133.1, 137.9, 138.5 ($C_{aromatic}$), 168.5 (C=NH) ppm.

[$PdCl_2$(HON=CMe_2)$_2$]:. $C_6H_{14}Cl_2N_2O_2Pd$ (323.5): calcd. C 22.28, H 4.36, N 8.66; found C 21.99, H 4.20, N 8.62. IR: $\tilde{\nu}$ = 3425 (OH), 1650 and 1622 (C=N–OH) cm^{-1}.

[$PdCl_2$(HON=C(Me)(Et))$_2$]: $C_8H_{18}Cl_2N_2O_2Pd$ (351.6): calcd. C 27.33, H 5.16, N 7.97; found C 27.45, H 5.23, N 8.03. IR: $\tilde{\nu}$ = 3191 (OH), 1666 (C=N–OH) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.31 (t, J_{HH} = 7.5 Hz, 3 H, CH_2CH_3), 2.07 (s, 3 H, CH_3), 3.05 (m, J_{HH} = 7.5 Hz, 2 H, CH_2CH_3) ppm. ^{13}C{^{1}H} NMR (400 MHz, $CDCl_3$): δ = 11.0 (CH_2CH_3), 16.43 (CH_3), 31.9 (CH_2CH_3), 168.1 (C=NOH) ppm.

Reactions of Cyanoguanidine HN=C(NH_2)N(H)C≡N (3) with $PdCl_2$ and Aliphatic Alcohols ROH (R = Me, Et, nPr, nBu) with the Formation of Asymmetrical (2-Amino-4-alkoxy-1,3,5-triazapentadienate)palladium(II) Complexes 4a–4d: $PdCl_2$ (177 mg,

1.00 mmol) and **3** (168 mg, 2.00 mmol) were added to the corresponding alcohol ROH (R = Me, Et, *n*Pr or *n*Bu) (5 mL) and the reaction mixture was refluxed or heated at 100 °C (in the case of *n*-butanol) for 12 h (homogenization of the reaction mixture was observed within ca. 1 h, giving a yellow solution). The solvent was then removed *in vacuo*, and the residue washed with three 10 mL portions of diethyl ether and then dried in air to give $[Pd(Htap)_2]Cl_2$ (**4′**). Recrystallization of **4′** from a methanol/chloroform (1:1) solution, with the addition of $nPrNH_2$ (2.00 equiv. to **4′**) gave the yellow palladium(II) complexes $[Pd(tap)_2]$ **4a**–**4d**. Compounds **4a**–**4d** were isolated as mixtures of isomers (see NMR spectroscopic data) and all attempts to obtain single crystals suitable for XRD analysis failed.

[Pd{HN=C(NH$_2$)NC(OMe)=NH}$_2$] (4a): Yield 75% (252 mg) based on $PdCl_2$. Decomp. temp. > 120 °C. $C_6H_{14}N_8O_2Pd$ (336): calcd. C 21.41, H 4.19, N 33.29; found C 21.76, H 4.27, N 33.36. ESI-MS: *m*/*z* (%) = 337 $[M + H]^+$. IR: $\tilde{\nu}$ = 3401 (NH), 1558, 1668 and 1686 (C=N) cm^{-1}. ^1H NMR (300 MHz, CD_3OD): δ = 3.99, 4.01, 4.04 (3 s, 6 H, C*H*$_3$) ppm. $^{13}C\{^1H\}$ NMR (400 MHz, CD_3OD): δ = 55.2, 55.6, 55.9 (*C*H$_3$), 152.4, 152.7, 154.1, 154.4, 154.6 (*C*=NH) ppm.

[Pd{HN=C(NH$_2$)NC(OEt)=NH}$_2$] (4b): Yield 77% (280 mg) based on $PdCl_2$. Decomp. temp. > 110 °C. $C_8H_{18}N_8O_2Pd$ (364): calcd. C 26.35, H 4.97, N 30.72; found C 26.66, H 5.13, N 31.05. ESI-MS: *m*/*z* (%) = 365 $[M + H]^+$. IR: $\tilde{\nu}$ = 3321 (NH), 1549 and 1689 (C=N) cm^{-1}. ^1H NMR (300 MHz, CD_3OD): δ = 1.40–1.46 (m, 6 H, C*H*$_3$), 4.28–4.46 (m, 4 H, C*H*$_2$) ppm. $^{13}C\{^1H\}$ NMR (400 MHz, CD_3OD): δ = 12.7, 12.8, 12.9, 12.9 (*C*H$_3$), 65.3, 65.8, 66.1, 66.2 (*C*H$_2$), 152.4, 152.7, 152.8, 153.4, 153.7, 153.8, 154.2, 154.5 (*C*=NH) ppm.

[Pd{HN=C(NH$_2$)NC(OPr)=NH}$_2$] (4c): Yield 73% (286 mg) based on $PdCl_2$. Decomp. temp. > 100 °C. $C_{10}H_{22}N_8O_2Pd$ (392): calcd. C 30.58, H 5.65, N 28.53; found C 30.67, H 5.95, N 28.77. ESI-MS: *m*/*z* (%) = 393 $[M + H]^+$. IR: $\tilde{\nu}$ = 3328 (NH), 1552 and 1689 (C=N) cm^{-1}. ^1H NMR (300 MHz, CD_3OD): δ = 0.91–1.07 (m, 6 H, C*H*$_3$), 1.51–1.85 (m, 4 H, CH_3CH_2), 4.19–4.36 (m, 4 H, OC*H*$_2$) ppm. $^{13}C\{^1H\}$ NMR (400 MHz, CD_3OD): δ = 8.95, 8.99, 9.02, 9.05, 9.22 (*C*H$_3$), 21.3, 21.4, 21.5, 25.3 (*C*H$_2$), 63.3, 70.7, 71.2, 71.4, 71.5, 71.6 (O*C*H$_2$), 152.4, 152.7, 152.8, 153.3, 153.5, 153.8, 153.9, 154.3, 154.6 (*C*=NH) ppm.

[Pd{HN=C(NH$_2$)NC(OBu)=NH}$_2$] (4d): Yield 78% (328 mg) based on $PdCl_2$. Decomp. temp. > 100 °C. $C_{12}H_{26}N_8O_2Pd$ (420): calcd. C 34.25, H 6.23, N 26.63; found C 34.37, H 6.55, N 26.87. ESI-MS: *m*/*z* (%) = 421 $[M + H]^+$. IR: $\tilde{\nu}$ = 3428 (NH), 1550 and 1682 (C=N) cm^{-1}. ^1H NMR [300 MHz, $CDCl_3$(90%), CD_3OD(10%)]: δ = 0.80–0.88 (m, 6 H, C*H*$_3$), 1.26–1.35 (m, 4 H, CH_3CH_2), 1.39–1.65 (m, 4 H, OCH_2CH_2), 4.22 (br. s, 4 H, OC*H*$_2$) ppm. $^{13}C\{^1H\}$ NMR [400 MHz, $CDCl_3$(90%), CD_3OD(10%)]: δ = 13.2, 13.3, 13.4, 13.5, 13.6 (*C*H$_3$), 18.5, 18.6, 18.6, 18.7, 19.2 (CH_3CH_2), 29.8, 30.0, 30.1, 31.7, 34.4 (OCH_2CH_2), 62.0, 62.1, 65.2, 70.1, 70.3 (O*C*H$_2$), 152.2, 152.9, 153.8, 154.2 (*C*=NH) ppm.

Reactions of Sodium Dicyanamide NaN(C≡*N*)$_2$ (5) with PdCl$_2$ and Aliphatic Alcohols ROH [R=Me, Et, Pr, (CH$_2$)$_2$OMe] with the Formation of Symmetrical (2,4-Dialkoxy-1,3,5-triazapentadienate)palladium(II) Complexes 6a–6d: $PdCl_2$ (177 mg, 1.00 mmol) and **5** (178 mg, 2.00 mmol) were added to the corresponding alcohol ROH [R = Me, Et, *n*Pr or $(CH_2)_2OMe$] (5 mL) and the reaction mixture was refluxed or heated at 100 °C (in the case of 2-methoxyethanol) for 12 h (homogenization of the reaction mixture was observed within ca. 1–2 h, giving a yellow solution). The solvent was then removed in vacuo, and the residue washed with three 10 mL portions of water (to remove the NaCl), and the remaining residue was crystallized from an acetone-water (10:1) mixture to give the corresponding symmetrical palladium(II) complexes **6a**–**6d**, which were isolated as mixtures of isomers (see NMR spectroscopic data). All attempts to obtain single crystals suitable for XRD analysis failed.

[Pd{HN=C(OMe)NC(OMe)=NH}$_2$] (6a): Yield 80% (293 mg) based on $PdCl_2$. Decomp. temp. > 250 °C. $C_8H_{16}N_6O_4Pd$ (366): calcd. C 26.20, H 4.40, N 22.92; found C 26.45, H 4.81, N 23.12. ESI-MS: *m*/*z* (%) = 367 $[M + H]^+$. IR: $\tilde{\nu}$ = 3359 (NH), 1613 (C=N) cm^{-1}. ^1H NMR (300 MHz, [D$_6$]DMSO): δ = 3.66–3.75 (m, 12 H, C*H*$_3$) ppm. $^{13}C\{^1H\}$ NMR (400 MHz, [D$_6$]DMSO): δ = 54.9, 55.0, 55.1, 55.6, 55.7 (*C*H$_3$), 160.9, 161.1, 161.3, 161.6, 162.0 (*C*=NH) ppm.

[Pd{HN=C(OEt)NC(OEt)=NH}$_2$] (6b): Yield 79% (333 mg) based on $PdCl_2$. Decomp. temp. > 230 °C. $C_{12}H_{24}N_6O_4Pd$ (422): calcd. C 34.09, H 5.72, N 19.88; found C 34.23, H 5.99, N 20.07. ESI-MS: *m*/*z* (%) = 423 $[M + H]^+$. IR: $\tilde{\nu}$ = 3371 (NH), 1610 (C=N) cm^{-1}. ^1H NMR (300 MHz, [D$_6$]DMSO): δ = 1.19–1.24 (m, 12 H, C*H*$_3$), 4.12–4.24 (m, 8 H, C*H*$_2$) ppm. $^{13}C\{^1H\}$ NMR (400 MHz, [D$_6$]DMSO): δ = 15.0, 15.1 (*C*H$_3$), 64.1, 64.2 (*C*H$_2$), 160.8, 161.1 (*C*=NH) ppm.

[Pd{HN=C(OPr)NC(OPr)=NH}$_2$] (6c): Yield 81% (387 mg) based on $PdCl_2$. Decomp. temp. > 230 °C. $C_{16}H_{32}N_6O_4Pd$ (478): calcd. C 40.13, H 6.74, N 17.55; found C 40.34, H 6.88, N 17.69. ESI-MS: *m*/*z* (%) = 479 $[M + H]^+$. IR: $\tilde{\nu}$ = 3376 (NH), 1608 and 1633 (C=N) cm^{-1}. ^1H NMR (300 MHz, [D$_6$]DMSO): δ = 0.87–0.93 (m, 12 H, C*H*$_3$), 1.57–1.65 (m, 8 H, CH_3CH_2), 4.02–4.18 (m, 8 H, OC*H*$_2$) ppm. $^{13}C\{^1H\}$ NMR (400 MHz, [D$_6$]DMSO): δ = 10.4, 10.6, 10.7 (*C*H$_3$), 21.9, 22.4, 22.5 (CH_3CH_2), 69.1, 69.7, 69.8, 70.0 (O*C*H$_2$), 160.9, 161.3 (*C*=NH) ppm.

[Pd{HN=C(O(CH$_2$)$_2$OMe)NC(O(CH$_2$)$_2$OMe)=NH}$_2$] (6d): Yield 83% (450 mg) based on $PdCl_2$. Decomp. temp. > 200 °C. $C_{16}H_{32}N_6O_8Pd$ (542): calcd. C 35.40, H 5.94, N 15.48; found C 35.67, H 5.89, N 15.77. ESI-MS: *m*/*z* (%) = 543 $[M + H]^+$. IR: $\tilde{\nu}$ = 3331 (NH), 1615 (C=N) cm^{-1}. ^1H NMR (300 MHz, [D$_6$]DMSO): δ = 3.26–3.27 (m, 12 H, C*H*$_3$), 3.53 (br. s, 8 H, CH_3OCH_2), 4.21 and 4.27 (2 br. s, 8 H, OC*H*$_2$) ppm. $^{13}C\{^1H\}$ NMR (400 MHz, [D$_6$]DMSO): δ = 58.5 (O*C*H$_3$), 66.6 (CH_3OCH_2), 70.7 (O*C*H$_2$), 160.5 (*C*=NH) ppm.

X-ray Structure Determination: Single crystals of **2c** were obtained as indicated above. Intensity data were collected on a Bruker AXS-KAPPA APEX II diffractometer with graphite monochromated Mo-K_α (λ 0.71073) radiation. Data were collected at 150 K with omega scans at 0.5° steps and full sphere of data was obtained. Cell parameters were retrieved with the Bruker SMART software and refined against all the observed reflections with the Bruker SAINT[34] program. An absorption correction was applied with SADABS.[34] The structure was solved by direct methods with the SHELXS–97 package[35] and refined with SHELXL–97.[36] Calculations were performed with WinGX software (version 1.80.03).[37] All hydrogen atoms were inserted into the model at calculated positions, except for H1 and H2 and the methanol hydrogen atom H10 that were located from the difference Fourier maps. Least square refinement, with anisotropic thermal parameters for all the non–hydrogen atoms and isotropic parameters for the hydrogen atoms, gave R_1 = 0.0196 [$I > 2\sigma(I)$] and R_1 = 0.0207 (all data). The maximum and minimum peaks in the final difference electron-density map are of 0.435 and –0.553 e Å^{-3}. Crystallographic data are listed in Table 1.

Table 1. Crystallographic data for **2c** (at 150 K).

	2c
Empirical formula	$C_{28}H_{20}Cl_4N_6Pd$, $2(CH_4O)$
Formula weight	752.78
Crystal system	triclinic
Space group	$P\bar{1}$
a [Å]	7.0242(2)
b [Å]	10.7629(2)
c [Å]	11.0018(3)
α [°]	79.901(1)
β [°]	75.572(3)
γ [°]	76.778(2)
V [Å^3]	777.956(36)
Z	1
ρ_{calc} [g cm^{-3}]	1.607
μ(Mo-K_α) [mm^{-1}]	0.979
F (000)	380
R_{int}	0.0200
Reflections collected/unique	10016/3436
Goodness of fit on F^2	1.093
R_1 [$I > 2\sigma(I)$]	0.0196 (0.0512)

CCDC-790158 contains 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.

Supporting Information (see also the footnote on the first page of this article): Fragment of the crystal packing diagram of **2c** showing the π···π stacking interactions within a supramolecular network structure of **2c**.

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