Journal of Organometallic Chemistry 696 (2011) 3513–3520

Contents lists available at SciVerse ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Microwave synthesis of bis(tetrazolato)-Pd^{II} complexes with PPh_3 and water-soluble 1,3,5-triaza-7-phosphaadamantane (PTA). The first example of C–CN bond cleavage of propionitrile by a Pd^{II} Centre

Jamal Lasri [a,*], María José Fernández Rodríguez [a,c], M. Fátima C. Guedes da Silva [a,b,*], Piotr Smoleński [a,d], Maximilian N. Kopylovich [a], João J.R. Fraústo da Silva [a], Armando J.L. Pombeiro [a,*]

[a] Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, Technical University of Lisbon, Av. Rovisco Pais, 1049-001 Lisbon, Portugal
[b] Universidade Lusófona de Humanidades e Tecnologias, Av. Campo Grande n° 376, ULHT Lisbon, 1749-024 Lisbon, Portugal
[c] Grupo de Química Organometálica, Departamento de Química Inorgánica, Facultad de Química, Universidad de Murcia, Apdo. 4021, Murcia 30071, Spain
[d] Faculty of Chemistry, University of Wrocław, ul. F. Joliot-Curie 14, 50-383 Wrocław, Poland

ARTICLE INFO

Article history:
Received 7 May 2011
Received in revised form
21 July 2011
Accepted 29 July 2011

Keywords:
1,3,5-Triaza-7-phosphaadamantane (PTA)
Azides
Nitriles
[2 + 3] Cycloadditions
Tetrazoles
Microwaves

ABSTRACT

[2 + 3] Cycloaddition reactions of the di(azido)-Pd^{II} complex *trans*-$[Pd(N_3)_2(PPh_3)_2]$ (**1**) with an organonitrile RCN (**2**), under heating for 12 h, give the bis(tetrazolato) complexes *trans*-$[Pd(N_4CR)_2(PPh_3)_2]$ (**3**) [R = Me (**3a**), Ph (**3b**), 4-ClC_6H_4 (**3c**), 4-FC_6H_4 (**3d**), 2-NC_5H_4 (**3e**), 3-NC_5H_4 (**3f**), 4-NC_5H_4 (**3g**)]. The reaction of *trans*-$[Pd(N_3)_2(PPh_3)_2]$ (**1**) with propionitrile (**2h**) also affords, apart from *trans*-$[Pd(N_4CEt)_2(PPh_3)_2]$ (**3h**), the unexpected mixed cyano-tetrazolato complex *trans*-$[Pd(CN)(N_4CEt)(PPh_3)_2]$ (**3h′**) which is derived from the reaction of the bis(tetrazolato) **3h** with propionitrile, with concomitant formation of 5-ethyl-1*H*-tetrazole, *via* a suggested unusual oxidative addition of the nitrile to Pd^{II}. The [2 + 3] cycloadditions of $[Pd(N_3)_2(PTA)_2]$ (**4**) (PTA = 1,3,5-triaza-7-phosphaadamantane) with RCN (**2**), under heating for 12 h, give the bis(tetrazolato) complexes *trans*-$[Pd(N_4CR)_2(PTA)_2]$ (**5**) [R = Ph (**5a**), 2-NC_5H_4 (**5b**), 3-NC_5H_4 (**5c**), 4-NC_5H_4 (**5d**)]. All these reactions are greatly accelerated by microwave irradiation (1 h, 125 °C, 300 W). Taking advantage of the hydrosolubility of PTA, a simple liberation of 5-phenyl-1*H*-tetrazole from the coordination sphere of *trans*-$[Pd(N_4CPh)_2(PTA)_2]$ (**5a**) was achieved. The complexes were characterized by IR, ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectroscopies, ESI^+-MS, elemental analyses and, for **3b**, also by X-ray structure analysis. Weak agostic interactions between the CH groups of the triphenylphosphines and the palladium(II) centre were found.

1. Introduction

Tetrazoles constitute an important class of compounds with applications in areas of coordination chemistry, materials science and medicinal chemistry [1–4]. They can be synthesized by [2 + 3] cycloaddition of an organonitrile with an azide, but only a few activated nitriles are known to undergo this reaction in an *inter*molecular fashion [5]. When the azide and the nitrile moieties are in the same molecule, the rate of cycloaddition can be greatly enhanced and polycyclic fused tetrazoles can be synthesized *via intra*molecular [2 + 3] cycloaddition [6]. The cycloaddition can also be promoted by using fluorous tin or trimethylsilyl azide [7], a strong Lewis acid [8], or a strong acidic media [9]. Sharpless et al. [10] improved the synthetic method by using a zinc salt as the Lewis acid and performing the reaction in aqueous medium. Amantini et al. [11] efficiently synthesized tetrazoles by reaction of trimethylsilyl azide with a nitrile using tetrabutylammonium fluoride as catalyst. The use of nanocrystalline ZnO as an heterogeneous catalyst [12] and microwave irradiation [13] to shorten the reaction time have also been reported. Phthalonitrile and terephthalonitrile react with azides in the presence of a metal chloride to give mono-tetrazoles [14].

Moreover, the formation of substituted tetrazoles can be achieved by using an azide coordinated to a transition metal and free organonitriles [15], isocyanides [16a] or isothiocynates [16b]. For example, we have shown [17] that the di(azido) complexes of the type *cis*-

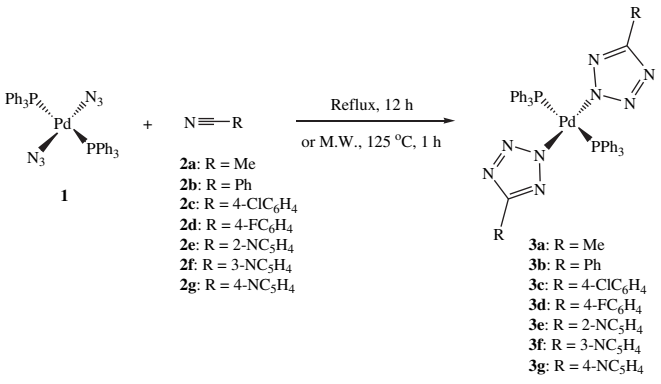
* Corresponding authors. Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, Technical University of Lisbon, Av. Rovisco Pais, 1049-001 Lisbon, Portugal. Tel.: +351 21 841 92 37.
E-mail addresses: jamal.lasri@ist.utl.pt (J. Lasri), fatima.guedes@ist.utl.pt (M. F. C. Guedes da Silva), pombeiro@ist.utl.pt (A.J.L. Pombeiro).

0022-328X/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2011.07.047

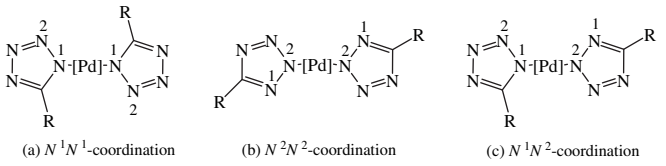
$[Pt(N_3)_2(PPh_3)_2]$ can react with nitriles NCR to give the bis(tetrazolato) compounds *trans*-$[Pt(N_4CR)_2(PPh_3)_2]$ from which the tetrazoles can be liberated. Very recently, we have reported that [2 + 3] cycloaddition of *cis*-$[Pt(N_3)_2(PPh_3)_2]$ with 4-cyanobenzaldehyde furnishes a (formylphenyl)tetrazolate complex that reacts with 2-dimethylaminoethylamine to give the corresponding Schiff base derivative, the latter undergoing hydrolysis in the presence of a metal salt, while the reactions of di(azido) complexes with dicyanobenzenes give (cyanophenyl)tetrazolate complexes [18]. In addition, the reactions of bis(tetrazolato)-Pt^{II} compounds with propionitrile furnish mono- or dicyano-complexes, *via* an unusual oxidative addition involving NC–C bond cleavage of one or two propionitrile molecules, respectively [17a–c]. On the other hand, in organometallic chemistry, activation of carbon–carbon bonds has been a popular topic and a few examples of NC–C bond cleavage in organonitriles by group 10 transition metal complexes are known [19] when the metals are in zero oxidation state. Moreover, the first example of C–C cleavage by oxidative addition of the C–CN bond to a Rh(I) centre has been recently reported [20].

Concerning the Pd^{II}-assisted [2 + 3] cycloadditions of azides to organonitriles, Beck and co-workers [21] have investigated the reaction of benzonitrile with $[Pd(N_3)_2(PPh_3)_2]$, by the traditional heating method, leading to *cis*-$[Pd(N_4CPh)_2(PPh_3)_2]$ and the structure of the cycloadduct was confirmed by X-ray diffraction analysis. In this case, both 5-phenyltetrazolato ligands are coordinated to Pd by the N^2 atom. On the other hand, the crystal structure of the related complex *cis*-$[Pd(N_4CMe)_2(PMe_2Ph)_2]$ demonstrates that both tetrazolato rings are N^1-bonded [22].

The coordination chemistry of the aqua-soluble phosphine 1,3,5-triaza-7-phosphaadamantane (PTA) and derived species has received an increased interest in recent years, in view of the good solubility of their complexes in water, thus making possible their efficient application in aqueous phase catalysis, as water-soluble antitumour agents and photoluminescent materials [23]. Four- and five-coordinated diazido-platinum(II) complexes *cis*-$[Pt(N_3)_2(PTA)_2]$ and $[Pt(N_3)_2(PTA)_3]$ were obtained by us [17a], in reaction of *cis*-$[Pt(N_3)_2(PPh_3)_2]$ with stoichiometric amounts of PTA. [2 + 3] Cycloadditions with organonitriles NCR give the bis(tetrazolato) *trans*-$[Pt(N_4CR)_2(PTA)_2]$ species [17a], from which the tetrazoles can be liberated and also conveniently isolated in a pure form on account, on one hand, of the high water solubility of the concomitantly formed PTA-platinum complex and, on the other hand, of the water insolubility of the tetrazole which spontaneously precipitates out from the solution. In this way, the 5-substituted tetrazoles were obtained and isolated as solids by an easy single-pot process upon simple treatment of the respective tetrazolato complexes with aqueous diluted HCl. However, the generality of this rather convenient preparative method was not established.



Scheme 1.



Scheme 2.

Thus, the aims of the current work are: i) to extend the number of *trans* tetrazolato-Pd^{II} complexes synthesized by [2 + 3] cycloaddition of a nitrile with an azide coordinated to a palladium(II) metal centre using PPh_3 and hydrosoluble PTA ligands; ii) to check if the mentioned reaction of azido-Pd^{II} species with propionitrile as a starting material involves carbon–carbon bond cleavage similarly to that observed for the tetrazolato-Pt^{II} complexes; iii) to investigate the effect of focused microwave irradiation (M.W.), since M.W. is an alternative way to the traditional refluxing method with the possible advantages [24] of increasing the selectivity and reducing the reaction time.

2. Results and discussion

2.1. Complexes with PPh_3

Treatment of the di(azido)-Pd^{II} complex *trans*-$[Pd(N_3)_2(PPh_3)_2]$ (**1**) with an organonitrile RCN (**2**), under heating for 12 h, gives the corresponding bis(tetrazolato) compounds *trans*-$[Pd(N_4CR)_2(PPh_3)_2]$ (**3**) [R = Me (**3a**), Ph (**3b**), 4-ClC_6H_4 (**3c**), 4-FC_6H_4 (**3d**), 2-NC_5H_4 (**3e**), 3-NC_5H_4 (**3f**), 4-NC_5H_4 (**3g**)], isolated as white or yellow crystalline solids in moderate yields (*ca.* 65–54%) (Scheme 1). When using a liquid organonitrile (**2a**–**2b**), this behaves also as the solvent whereas, in the case of solid nitriles (**2c**–**2g**), dimethylformamide (DMF) is the solvent used. The reactions are undertaken either in solvent refluxing conditions (for 12 h) by conventional heating or under focused microwave (M.W.) irradiation (1 h, 125 °C, 300 W). The latter method greatly accelerates the reactions, leading only in 1 h to yields that are comparable to those obtained after 12 h under conventional heating. The

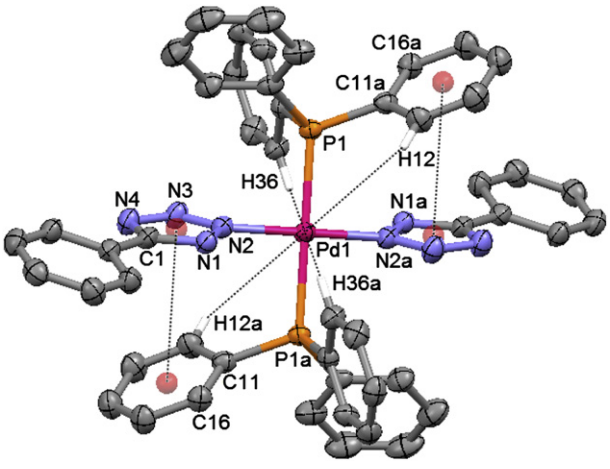
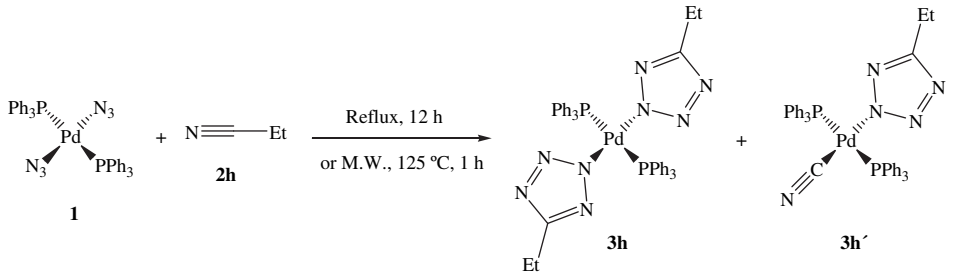


Fig. 1. Thermal ellipsoid plot, drawn at the 50% probability level, of the *trans* 5-phenyltetrazolato palladium(II) complex **3b** with atomic numbering scheme. Selected bond lengths (Å) and angles (°): Pd1–P1 2.3469(4), Pd1–N2 1.9953(15), P1–Pd1–N2 91.49(4), N2–Pd1–P1a 88.50(4). π···π and agostic interactions (shown as dashed lines): *centroid*···*centroid* 3.6536(12) Å; *d*(H12···Pd1) 3.40 Å, ∠(C12–H12···Pd1) 107.09°; *d*(H36···Pd1) 2.93 Å, ∠(C36–H36···Pd1) 119.51°. Hydrogen atoms not involved in fundamental interactions are omitted for clarity. Symmetry code to generate equivalent atoms: a) −x,1−y,1−z.



Scheme 3.

tetrazolato-Pd^{II} complexes are formed *via* [2 + 3] cycloaddition of the organonitriles with the ligated azides.

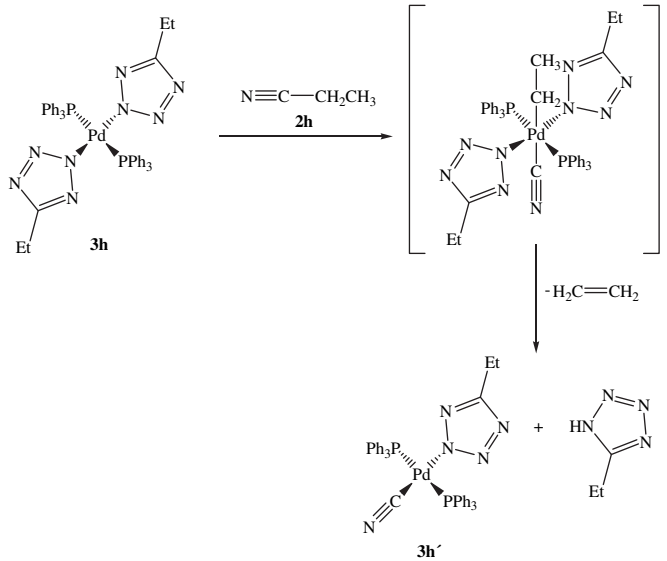
The obtained complexes **3** were characterized by elemental analyses, IR and ^{1}H, $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$ spectroscopies, and ESI^{+}-MS. Their IR spectra do not show the typical azide band at *ca.* 2036 cm^{-1} and display a new strong band within the 1615–1638 cm^{-1} range due to the tetrazole ring, in agreement with the literature [17]. No band assigned to N–H stretching or bending was observed, in contrast to typical bands of triphenylphosphine ligands at *ca.* 1436 cm^{-1} and 693 cm^{-1}, which are also displayed by the starting complex **1**. The $^{13}C\{^{1}H\}$ NMR spectra of complexes **3** show the characteristic signal in the 151–164 ppm range due to the carbon of the tetrazolato ring.

Moreover, the NMR spectra of **3** often display more than one peak for each particular type of atoms, what can be accounted for by linkage isomerism due to the possible ambidentate behaviour of the tetrazolate ligand which, in principle, can bind to the metal through either the N^1 or the N^2 atom leading to the possibility of existence of several isomers (N^1N^1, N^2N^2 and N^1N^2 combinations), in addition to *cis*- and *trans*-isomers [17c] (Scheme 2). However, N^2N^2-coordinated is sterically favourable and is that established in the solid state by X-ray diffraction (see below).

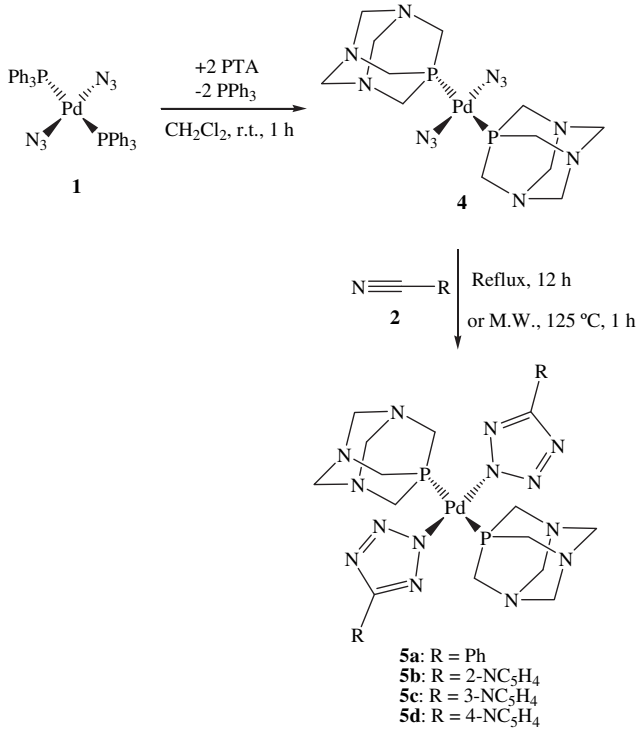
For instance, the ^{1}H NMR spectrum of *cis*/*trans*-$[Pd(N_4CMe)_2(PPh_3)_2]$ (**3a**) shows four signals for the methyl protons at δ 1.88, 2.01, 2.21 and 2.24, whereas in the $^{13}C\{^{1}H\}$ NMR spectrum four resonances for the methyl carbon are detected at δ 9.93, 9.95, 10.60 and 10.69, suggesting the presence of four isomers in solution. In the $^{31}P\{^{1}H\}$ NMR spectrum, also four signals were observed at δ 17.65, 18.08, 23.02 and 29.19. Those four isomers concern **3a** obtained under M.W. irradiation (1 h, 125 °C, 300 W). Nevertheless, the $^{31}P\{^{1}H\}$ NMR spectrum of **3a** synthesized by conventional heating methods (reflux, 12 h) shows only three signals at δ 17.65, 23.02 and 29.19, probably due to the conversion of the *cis* isomer ($^{31}P\{^{1}H\}$ NMR δ 18.08) into the thermodynamically more stable *trans* form.

In our previous work [17c], we found that the 5-phenyltetrazolato-Pt^{II} complex *trans*-$[Pt(N_4CPh)_2(PPh_3)_2]$ exhibits one signal at δ 17.11 ($J_{Pt-P} = 2720$ Hz) in the $^{31}P\{^{1}H\}$ NMR spectrum, due to the presence of only one isomer in solution. Moreover, the single *trans* isomer was prepared by both conventional heating methods and under M.W. irradiation. However, the $^{31}P\{^{1}H\}$ NMR spectrum of the analogous Pd^{II} complex $[Pd(N_4CPh)_2(PPh_3)_2]$ (**3b**) prepared under M.W. irradiation (1 h, 125 °C, 300 W) shows three resonances at δ 18.40, 22.82 and 29.25. When **3b** is prepared under solvent refluxing conditions (12 h), only one signal at δ 18.40 is observed in its $^{31}P\{^{1}H\}$ NMR spectrum. This is indicative that in this case the possible *cis*/*trans*-isomers (with different coordination modes) can also convert into the thermodynamically more stable *trans* one, and in order to avoid steric congestion, both the bulky phenyltetrazolato rings are conceivably coordinated to the metal centre only by the N^2 atom [17c].

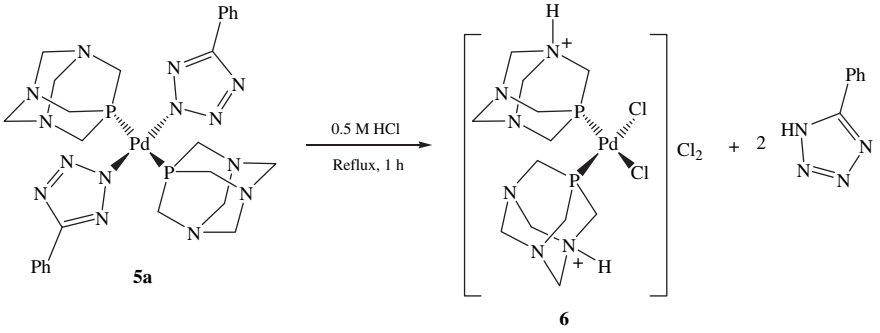
The single crystal X-ray diffraction analysis of **3b** confirms the proposed structure. The ORTEP drawing in Fig. 1 clearly displays the N^2N^2-coordination mode of the tetrazolato ligands. The metal lies on a crystallographic inversion point in a slightly distorted square-



Scheme 4.



Scheme 5.



Scheme 6.

planar geometry with the two tetrazolato rings in mutually *trans* position. The tetrazole rings are essentially planar and their phenyl moieties are twisted out of the N_4C plane with a dihedral angle of 16.43°. Moreover, the phenyl substituents attached to the tetrazolato rings are oriented in the opposite direction (*anti* orientation), while the phosphine groups take a staggered conformation. The Pd–N bond distance (1.9953(15) Å) is comparable with those found (*ca.* 2.08 Å) in other bis-tetrazolato Pd(II) complexes [21,22], and is somewhat shorter than the sum of the metal and nitrogen covalent radii (1.39 + 0.68 Å) suggesting a partial π-character in this bond. The Pd–P bond distance (2.3469(4) Å) is also shorter than the metal and phosphorus covalent radii (1.39 + 1.05 Å), what is commonly found in mutually *trans*-phosphines.

The complex molecule conformation is stabilized by intramolecular π···π interaction involving the tetrazole ring and the phosphine C11 > C16 phenyls (*centroid*···*centroid* distance of 3.6536(12) Å). Moreover, reasonably strong intramolecular agostic interactions were also found, involving the metal and aromatic phosphine hydrogens (H12···Pd1 3.40 Å, C12–H12···Pd1 107.09°; H36···Pd1 2.93 Å, C36–H36···Pd1 119.51°). Therefore, the above considered square-planar geometry around the Pd(II) centre in **3b** can be envisaged as a distorted octahedron if the longer agostic Pd1···H interactions are taken into consideration.

Similarly to the case of platinum(II) complexes [17c], the reaction of propionitrile (**2h**) with *trans*-[$Pd(N_3)_2(PPh_3)_2$] (**1**), by refluxing for 12 h or under M.W. irradiation (1 h, 125 °C, 300 W), gives not only the expected *trans*-[$Pd(N_4CEt)_2(PPh_3)_2$] (**3h**), but also the cyano-complex *trans*-[$Pd(CN)(N_4CEt)(PPh_3)_2$] (**3h′**) (Scheme 3).

The formation of **3h′** is believed to proceed *via* the bis(tetrazolato) compound **3h**, propionitrile being the precursor of the cyanide ligand. The initial formation of complex **3h** *via* the [2 + 3] cycloaddition of the propionitrile (as observed with the other nitriles) with a ligated azide is kinetically driven and such a complex, upon prolonged reaction time, converts into the thermodynamically more stable cyano-complex **3h′**.

A possible pathway for the unexpected conversion of **3h** into the corresponding cyano-complex **3h′** is proposed in Scheme 4. It involves an oxidative addition of propionitrile (which thus undergoes NC–C bond cleavage [17c,19,20]) to Pd^{II} to give a cyanoethyl-Pd^{IV} intermediate, followed by β-elimination from the ethyl ligand to form ethylene,[1] and reductive elimination of 5-ethyl-1*H*-tetrazole, which could be isolated and characterized by IR, ^1H and $^{13}C\{^1H\}$ NMR spectroscopies and ESI^+-MS.

[1] Ethylene cannot be detected in solution by NMR on account of its too low amount relatively to that of the propionitrile solvent bearing the interfering strong propyl NMR resonances. However, the formation of ethylene is corroborated by the stoichiometry of the reaction (Scheme 4).

Complex **3h′** cannot be isolated in a pure form, by thermal heating or under M.W. irradiation, and a mixture of **3h** and **3h′** was obtained. The mixture has been characterized by IR and ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectroscopies, and ESI^+-MS. The IR spectrum of the mixture shows a strong band at 1630 cm^{-1} due to the tetrazole rings and a band at 2139 cm^{-1} is assigned to ν(CN) of the cyano ligand (complex **3h′**). The $^{13}C\{^1H\}$ NMR resonances at 126.9 and 166.5 ppm confirm the presence of cyano and tetrazolato ligands, respectively [17]. The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture shows two resonances at δ 23.0 and 30.2 (3:1 relative intensities).

2.2. Complexes with PTA

As mentioned above, PTA can be an alternative and useful phosphine for further applications in aqua-systems. Hence, we decided to synthesize analogous complexes with PTA instead of PPh_3, and to carry out the liberation of ligated tetrazole in aqueous medium. The reaction of stoichiometric quantities of PTA and *trans*-[$Pd(N_3)_2(PPh_3)_2$] (**1**) (Pd:PTA = 1:2) in CH_2Cl_2 at room temperature leads to the precipitation of [$Pd(N_3)_2(PTA)_2$] (**4**) as an yellow microcrystalline solid in 60% yield (Scheme 5). Complex **4** is stable in the solid state and in solution. The bis(tetrazolato) complexes *trans*-[$Pd(N_4CR)_2(PTA)_2$] (**5**) [R = Ph (**5a**), 2-NC_5H_4 (**5b**), 3-NC_5H_4 (**5c**) or 4-NC_5H_4 (**5d**)] were synthesized by reaction of [$Pt(N_3)_2(PTA)_2$] (**4**) with the appropriate organonitrile NCR (**2**), and the reaction is accelerated by M.W. (125 °C, 1 h, 300 W). They were isolated in moderate yields (*ca.* 50–55%) as yellow powders (Scheme 5). The tetrazolato-Pd^{II} complexes **5a**–**5d** are formed *via* [2 + 3] cycloaddition of the organonitriles with the ligated azides and they are stable in the solid state. Complex **5a** is soluble in middle polar solvents, such as $CHCl_3$ and CH_2Cl_2, sparingly soluble in polar ones such as H_2O, MeOH, MeCN and Me_2SO, while compounds **5b**–**5d** are insoluble in common organic solvents and water.

Compounds **4** and **5** have been characterized by elemental analyses, IR and NMR spectroscopies. The IR spectrum of **4** exhibits the typical azide band (2037 cm^{-1}). The $^{13}C\{^1H\}$ NMR spectrum of **5a** shows the characteristic signal at 165 ppm due to the tetrazolato ring carbon. The ^1H NMR spectra of **4** and **5a** at room temperature show two types of methylene protons. One of them, P–CH_2–N, occurs as a broad singlet at δ 4.35 and 4.20, respectively. The second type, N–CH_2–N, displays for **4** and **5a** an AB spin system centred at δ 4.47 and 4.44 (J_{AB} = 13 and 15 Hz), respectively, assigned to the N–CH_{ax}–N and the N–CH_{eq}–N protons [23]. The $^{31}P\{^1H\}$ NMR spectra of **4** and **5a** display singlets at −30.2 and −47.3 ppm, respectively.

Liberation of the ligated tetrazole from the coordination sphere of the bis(tetrazolato)-Pd^{II} complex *trans*-[$Pd(N_4CPh)_2(PTA)_2$] (**5a**)

Table 1
Crystal data and structure refinement details for *trans*-$[Pd(N_4CPh)_2(PPh_3)_2]$ (**3b**).

Compound	**3b**
empirical formula	$C_{50}H_{40}N_8P_2Pd$
fw	921.24
λ (Å)	
cryst syst	Triclinic
space group	P-1
a (Å)	8.7688 (3)
b (Å)	11.7142 (4)
c (Å)	11.7416 (4)
α (deg)	68.890 (2)
β (deg)	76.809 (3)
γ (deg)	72.483 (2)
V (Å^3)	1063.20 (7)
Z	1
ρ_{calcd} (g/cm^3)	1.439
μ (Mo-Kα) (mm^{-1})	0.558
no. of collected reflns	25117
no. of unique reflns	6886
R_{int}	0.0403
Final $R1$,[a] $wR2$[b] ($I \geq 2\sigma$)	0.0373, 0.0821
GOF on F^2	1.049

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

was achieved by treatment with aqueous HCl, similarly to the previously described [17a] reaction of the platinum compounds *trans*-$[Pt(N_4CR)_2(PTA)_2]$ (R = Ph, 4-ClC_6H_4 or 3-NC_5H_4) with diluted HCl (Scheme 6). The method is simple and convenient in terms of providing an easy separation of the tetrazole products. It involves refluxing a suspension of **5a** in aqueous 0.5 M HCl for 1 h. The precipitate formed during the reaction was separated by filtration and a white solid was then extracted with chloroform, and shown (by IR and NMR spectroscopies) to be the corresponding 5-phenyl-1*H*-tetrazole (yield *ca.* 50%) [17a]. The remaining white-yellow precipitate is completely insoluble in chloroform, and, by IR (KBr) and elemental analysis, was shown to be $[PdCl_2(PTA\text{-}H)_2]Cl_2$ (**6**) (PTA-H = *N*-protonated PTA cation). Its insolubility in common solvents precluded NMR analysis, but it is deprotonated by base (NaOH) to give the expected known $[PdCl_2(PTA)_2]$ [28], as proved by $^{31}P\{^1H\}$ NMR in a D_2O solution with NaOH.

3. Conclusions

In this work we have shown that the di(azido) compounds *trans*-$[Pd(N_3)_2(PPh_3)_2]$ and $[Pd(N_3)_2(PTA)_2]$ (which are hydrosoluble) are good starting materials for a variety of *trans* bis(5-substituted tetrazolato)-Pd^{II} complexes derived upon [2 + 3] cycloadditions with nitriles. We also found that propionitrile, on reaction with *trans*-$[Pd(N_4CEt)_2(PPh_3)_2]$ (**3h**), undergoes an unusual NC–C bond cleavage behaving as a source of a cyano ligand to give *trans*-$[Pd(CN)(N_4CEt)(PPh_3)_2]$ (**3h′**) and 5-ethyl-1*H*-tetrazole, *via* a suggested unusual oxidative addition of this nitrile to Pd^{II} followed by β-H-elimination from the derived ethyl ligand and reductive elimination of the tetrazole. This provides, to our knowledge, the first example of synthesis of a mixed cyano-tetrazolato palladium(II) complex, which is obtained by C–C bond cleavage of an organonitrile.

The *trans* arrangement of the two tetrazolato ligands appears to be the most favourable one, in contrast to the previous reports [21,22,25], as clearly established by X-ray diffraction analysis. Different linkage isomers, on account of the ambidentate character of the tetrazolato ligand that can coordinate by either the N^1 or the N^2 mode, have been spectroscopically detected in solution, but the resolved crystal structure of complex **3b** shows that, in the solid state, the mode of tetrazolato binding is through the N^2atom. The multifunctionality of the tetrazolato and of the cyano-tetrazolato complexes provides a potential convenient entry to polynuclear assemblies which deserves to be explored.

Taking advantage of the hydro-solubility of PTA, a simple liberation of the ligated tetrazolate from the coordination sphere of *trans*-$[Pd(N_4CPh)_2(PTA)_2]$ was achieved, similarly to related Pt(II) complexes, what constitutes a convenient metal-mediated synthetic method for substituted tetrazoles.

Finally, microwave irradiation promotes the [2 + 3] cycloaddition of organonitriles with azide, resulting in a pronounced shortening of the reaction time relatively to the conventional heating.

4. Experimental

4.1. General procedures, materials and measurements

Solvents were purchased from Aldrich and dried by usual procedures. *Trans*-$[Pd(N_3)_2(PPh_3)_2]$ (**1**) [26] and PTA [27] were prepared according to published procedures. C, H and N elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra (in $CDCl_3$ or DMSO-d_6) were measured on a Bruker Avance II 300 and 400 MHz (UltraShield™ Magnet) spectrometer at ambient temperature. ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ chemical shifts (δ) are expressed in ppm relative to $Si(Me)_4$ (^1H and $^{13}C\{^1H\}$) or 85% H_3PO_4 (^{31}P). Infrared spectra (4000–400 cm^{-1}) were recorded on a Bio-Rad FTS 3000MX instrument in KBr pellets and the wavenumbers are in cm^{-1}. 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 solutions 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 was used as nebulizer gas at a pressure of 35 psi. Scanning was performed from m/z = 50 to 1500. The microwave irradiation experiments were undertaken in a focused microwave CEM Discover reactor (10 mL, 13 mm diameter, 300 W) which is fitted with a rotational system and an IR detector of temperature.

4.2. Preparations

4.2.1. Complexes *3a–3b*

These complexes can be prepared by two different methods. The first one by refluxing the solution of the starting complex *trans*-$[Pd(N_3)_2(PPh_3)_2]$ (**1**) in the respective nitrile, and the second one by using focused microwave irradiation.

(i) **By refluxing**: A solution of *trans*-$[Pd(N_3)_2(PPh_3)_2]$ (**1**) (20.0 mg, 0.028 mmol) in acetonitrile (**2a**) or benzonitrile (**2b**) (4 mL) was refluxed or heated at 100 °C (in the case of benzonitrile) for 12 h whereupon the solvent was removed *in vacuo*. The residue was washed with diethyl ether to obtain a white or yellow semi-crystalline solid. Recrystallization from a chloroform/diethyl ether mixture gave complexes **3a** or **3b**, respectively. Single crystals of complex **3b** suitable for X-ray structural analysis were obtained by slow evaporation of a chloroform solution.

(ii) **By focused microwave irradiation**: In this method, identical amounts of the reagents described above were added to a cylindrical Pyrex tube which was then placed in the focused microwave reactor. The system was left under irradiation for 1 h at 125 °C. The solvent was then removed *in vacuo* and the resulting solid residue was treated in a manner similar to that described above to obtain a white crystalline solid of **3a** or **3b.**

*4.2.2. Complexes **3c**–**3g***

(i) **By refluxing**: To a 4 mL solution of *trans*-[Pd(N$_3$)$_2$(PPh$_3$)$_2$] (**1**) (20.0 mg, 0.028 mmol) in DMF was added 4-chlorobenzonitrile (**2c**), 4-fluorobenzonitrile (**2d**), 2-cyanopyridine (**2e**), 3-cyanopyridine (**2f**) or 4-cyanopyridine (**2g**) (0.280 mmol). The resulting mixture was refluxed for 12 h. The solution became turbid as the product started to precipitate. The mixture was cooled and the solid was filtered off, washed several times with 5 mL portions of diethyl ether, and dried *in vacuo* to give the final complex **3c**, **3d**, **3e**, **3f** or **3g**, respectively.

(ii) **By focused microwave irradiation**: Complexes **3c**–**3g** were also prepared by dissolving the above mentioned amounts of the reagents in 4 mL of DMF and irradiating the solution with focused microwave for 1 h at 125 °C. They precipitated as white or yellow solids which were washed several times with diethyl ether and dried *in vacuo*.

*4.2.3. Trans-[Pd(N$_4$CMe)$_2$(PPh$_3$)$_2$] (**3a**)*

60% (method i) and 58% (method ii) yield. IR (cm^{-1}): 693 and 1436 (PPh$_3$), 1630 (C═N). ^{1}H NMR (CDCl$_3$), δ 1.88, 2.01, 2.21 and 2.24 (6H, CH$_3$), 7.30–7.72 (m, 30H, aromatic). ^{13}C{^{1}H} NMR (CDCl$_3$), δ 9.93, 9.95, 10.60 and 10.69 (CH$_3$), 125.44–135.64 (C$_{aromatic}$), 151.44, 156.74, 157.01 and 161.27 (C═N). ^{31}P{^{1}H} NMR (CDCl$_3$), δ 17.65, *18.08*, 23.02 and 29.19 (the signal in *italic* was not observed when the complex was prepared under refluxing conditions). Anal. Calcd for PdC$_{40}$H$_{36}$N$_8$P$_2$: C, 60.27; H, 4.55, N, 14.06. Found: C, 60.51; H, 4.31; N, 14.30. ESI$^+$-MS, *m*/*z* 798 [M + 1]$^+$.

*4.2.4. Trans-[Pd(N$_4$CPh)$_2$(PPh$_3$)$_2$] (**3b**)*

58% (method i) and 62% (method ii) yield. IR (cm^{-1}): 693 and 1437 (PPh$_3$), 1638 (C═N). ^{1}H NMR (CDCl$_3$), δ 7.21–7.59 (m, 40H, aromatic). ^{13}C{^{1}H} NMR (CDCl$_3$), δ 126.24–135.52 (C$_{aromatic}$), 164.54 (C═N). ^{31}P{^{1}H} NMR (CDCl$_3$), δ *18.40*, 22.82 and 29.25 (only the signal in *italic* was observed when the complex was obtained under refluxing conditions). Anal. Calcd for PdC$_{50}$H$_{40}$N$_8$P$_2$: C, 65.19; H, 4.38; N, 12.16. Found: C, 65.56; H, 4.19; N, 11.93. ESI$^+$-MS, *m*/*z* 922 [M + 1]$^+$.

*4.2.5. Trans-[Pd(N$_4$C(4-ClC$_6$H$_4$))$_2$(PPh$_3$)$_2$] (**3c**)*

55% (method i) and 58% (method ii) yield. IR (cm^{-1}): 691 and 1438 (PPh$_3$), 1630 (C═N). ^{1}H NMR (CDCl$_3$), δ 7.19–7.79 (m, 38H, aromatic). ^{13}C{^{1}H} NMR (CDCl$_3$), δ 127.39–135.63 (C$_{aromatic}$). The signal of the imine moiety (*C*═N) could not be observed even after more scans and/or by using DMSO-d_6 as solvent. ^{31}P{^{1}H} NMR (CDCl$_3$), δ 18.53, 20.05, 22.91 and 29.23 (only one signal of ^{31}P{^{1}H} NMR in DMSO-d_6 at δ 25.65 was observed when the complex was obtained under refluxing conditions). Anal. Calcd for PdC$_{50}$H$_{38}$N$_8$P$_2$Cl$_2$: C, 60.65; H, 3.87; N, 11.32. Found: C, 60.41; H, 3.71; N, 11.50. ESI$^+$-MS, *m*/*z* 991 [M + 1]$^+$.

*4.2.6. Trans-[Pd(N$_4$C(4-FC$_6$H$_4$))$_2$(PPh$_3$)$_2$] (**3d**)*

54% (method i) and 56% (method ii) yield. IR (cm^{-1}): 694 and 1451 (PPh$_3$), 1615 (C═N). ^{1}H NMR (DMSO-d_6), δ 7.26–7.71 (m, 38H, aromatic). ^{13}C{^{1}H} NMR (DMSO-d_6), δ 129.17–133.71 (C$_{aromatic}$), 161.11, 161.83 and 162.41 (C═N). ^{31}P{^{1}H} NMR (DMSO-d_6), δ 25.50. Anal. Calcd for PdC$_{50}$H$_{38}$N$_8$P$_2$F$_2$: C, 62.74; H, 4.00; N, 11.71. Found: C, 62.41; H, 4.21; N, 11.49. ESI$^+$-MS, *m*/*z* 958 [M + 1]$^+$.

*4.2.7. Trans-[Pd(N$_4$C(2-NC$_5$H$_4$))$_2$(PPh$_3$)$_2$] (**3e**)*

60% (method i) and 62% (method ii) yield. IR (cm^{-1}): 719 and 1450 (PPh$_3$), 1619 (C═N). ^{1}H NMR (CDCl$_3$), δ 7.34–7.75 (m, 38H, aromatic). The ^{13}C{^{1}H} NMR spectrum was not possible to obtain due to the very poor solubility of the complex **3e** in common solvents (CDCl$_3$, MeOD-d_4 or DMSO-d_6). ^{31}P{^{1}H} NMR (CDCl$_3$), δ 23.50. Anal. Calcd for PdC$_{48}$H$_{38}$N$_{10}$P$_2$: C, 62.44; H, 4.15; N, 15.17. Found: C, 62.33; H, 4.44; N, 15.45. ESI$^+$-MS, *m*/*z* 924 [M + 1]$^+$.

*4.2.8. Trans-[Pd(N$_4$C(3-NC$_5$H$_4$))$_2$(PPh$_3$)$_2$] (**3f**)*

61% (method i) and 60% (method ii) yield. IR (cm^{-1}): 693 and 1436 (PPh$_3$), 1630 (C═N). ^{1}H NMR (CDCl$_3$), δ 7.44–7.72 (m, 38H, aromatic). ^{13}C{^{1}H} NMR (CDCl$_3$), δ 128.40–134.02 (C$_{aromatic}$). The signal of the imine moiety (*C*═N) could not be observed even after more scans. ^{31}P{^{1}H} NMR (CDCl$_3$), δ 29.25. Anal. Calcd for PdC$_{48}$H$_{38}$N$_{10}$P$_2$: C, 62.44; H, 4.15; N, 15.17. Found: C, 62.38; H, 4.55; N, 15.37. ESI$^+$-MS, *m*/*z* 924 [M + 1]$^+$.

*4.2.9. Trans-[Pd(N$_4$C(4-NC$_5$H$_4$))$_2$(PPh$_3$)$_2$] (**3g**)*

63% (method i) and 65% (method ii) yield. IR (cm^{-1}): 694 and 1436 (PPh$_3$), 1619 (C═N). ^{1}H NMR (CDCl$_3$), δ 7.19–7.67 (m, 38H, aromatic). ^{13}C{^{1}H} NMR (CDCl$_3$), δ 120.80–150.15 (C$_{aromatic}$), 161.67, 161.87, 162.09 and 162.50 (C═N). ^{31}P{^{1}H} NMR (CDCl$_3$), δ 18.96, *24.22*, 26.34 and 29.41 (only the signal in *italic* was observed when the complex was obtained under refluxing conditions). Anal. Calcd for PdC$_{48}$H$_{38}$N$_{10}$P$_2$: C, 62.44; H, 4.15; N, 15.17. Found: C, 62.41; H, 4.20; N, 15.27. ESI$^+$-MS, *m*/*z* 924 [M + 1]$^+$.

*4.2.10. Preparation of trans-[Pd(N$_4$CEt)$_2$(PPh$_3$)$_2$] (**3h**), trans-[Pd(CN)(N$_4$CEt)(PPh$_3$)$_2$] (**3h′**) and 5-ethyl-1H-tetrazole*

A solution of *trans*-[Pd(N$_3$)$_2$(PPh$_3$)$_2$] (**1**) (20.0 mg, 0.028 mmol) in propionitrile (**2h**) (4 mL) was refluxed for 12 h or irradiated under M.W. (1 h, 125 °C, 300 W) whereupon the solvent was removed *in vacuo*. The white solid (**3h** and **3h′**) was filtered off and washed with diethyl ether for several times. The mother liquor was evaporated to dryness and the resulting compound was identified as 5-ethyl-1*H*-tetrazole.

*4.2.11. Trans-[Pd(N$_4$CEt)$_2$(PPh$_3$)$_2$] (**3h**) and trans-[Pd(CN)(N$_4$CEt)(PPh$_3$)$_2$] (**3h′**)*

IR (cm^{-1}): 2139 (C≡N), 1630 (C═N). ^{1}H NMR (CDCl$_3$), δ 0.84–1.33 (m, 9H, CH$_3$), 2.18–2.37 (m, 6H, CH$_2$), 7.35–7.69 (m, 60H, aromatic). ^{13}C{^{1}H} NMR (CDCl$_3$), δ 10.87, 12.41 and 12.55 (CH$_3$), 18.64 and 18.78 (CH$_2$), 126.97 (C≡N), 127.59–134.39 (C$_{aromatic}$), 166.53 (C═N). ^{31}P{^{1}H} NMR (CDCl$_3$), δ 23.0 and 30.2. ESI$^+$-MS, *m*/*z* 825 [M + 1]$^+$ (**3h**) and 755 [M + 1]$^+$ (**3h′**).

4.2.12. 5-ethyl-1H-tetrazole

IR (cm^{-1}): 1638 (C═N). ^{1}H NMR (CDCl$_3$), δ 1.30 (t, J_{HH} = 7.6 Hz, 3H, CH$_3$), 2.87 (q, J_{HH} = 7.6 Hz, 2H, CH$_2$).^{13}C{^{1}H} NMR (CDCl$_3$), δ 14.16 (CH$_3$), 19.33 (CH$_2$), 159.86 (C═N). ESI$^+$-MS, *m*/*z* 99 [M + 1]$^+$.

*4.2.13. [Pd(N$_3$)$_2$(PTA)$_2$]·CH$_2$Cl$_2$, (**4**)·CH$_2$Cl$_2$*

To a solution of *trans*-[Pd(N$_3$)$_2$(PPh$_3$)$_2$] (**1**) (200.0 mg, 0.28 mmol) in dichloromethane (25 mL), PTA (88.0 mg, 0.56 mmol) was added. The mixture was stirred for *ca.* 1 h under dinitrogen at room temperature. The yellow precipitate was separated from the brown solution by filtration, washed with chloroform (3 × 10 mL) and dried *in vacuo* to afford complex **4** as a yellow microcrystalline solid. Yield of **4**·CH$_2$Cl$_2$ 60% (85 mg). Complex **4** is soluble in H$_2$O and DMSO, slightly soluble in MeOH and CH$_2$Cl$_2$, and insoluble in C$_6$H$_6$. [Pd(N$_3$)$_2$(PTA)$_2$]·CH$_2$Cl$_2$, C$_{13}$H$_{26}$Cl$_2$N$_{12}$P$_2$Pd (589.7): calcd. C 26.48, N 28.50, H 4.44; found C 26.00, N 29.11, H 4.45. IR (KBr): 2930 (s br) ν(CH), 2037 (s br) ν(N$_3$), 1278 (m), 1242 (s), 1099 (m), 1014 (s), 972 (s), 943 (s), 904 (m), 805 (m), 741 (m), 582 (m) (PTA) cm−^{1}. ^{1}H NMR (DMSO-d_6): δ 5.75 (s, CH$_2$Cl$_2$, 2H), 4.53 H^A and 4.41 H^B (J_{AB} = 13.0 Hz, NCH^{A}H^{B}N, 12H), 4.35 (s, PCH$_2$N, 12H). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 72.6 (s, N–CH$_2$–N, PTA), 55.8 (s, CH$_2$Cl$_2$), 52.3 (br. s, P–CH$_2$–N, PTA). ^{31}P{^{1}H} NMR (DMSO-d_6): δ −30.2 (s).

*4.2.14. Trans-[Pd(N$_4$CPh)$_2$(PTA)$_2$]·PhCN, (**5a**)·PhCN*

A mixture of [Pd(N$_3$)$_2$(PTA)$_2$]·CH$_2$Cl$_2$ (**4**·CH$_2$Cl$_2$) (59.0 mg, 0.10 mmol) and PhCN (5 mL, 48.5 mmol) was added to a cylindrical Pyrex tube which was then placed in the focused microwave reactor. The system was left under irradiation for 1 h at 125 °C (the same product was obtained when the mixture of reagents was refluxed for 12 h). After reaction, the excess of PhCN was removed *in vacuo* and the resulting residue was washed repeatedly with 10 mL portions of diethyl ether. Recrystallization from a dichloromethane/diethyl ether mixture gave yellow microcrystals of *trans*-[Pd(N$_4$CPh)$_2$(PTA)$_2$]·PhCN (**5a**·PhCN). Yield 55% (45 mg). Complex **5a** is soluble in DMSO, CHCl$_3$ and CH$_2$Cl$_2$, sparingly soluble in H$_2$O, and insoluble in diethyl ether and C$_6$H$_6$. *Trans*-[Pd(N$_4$CPh)$_2$(PTA)$_2$]·PhCN, C$_{33}$H$_{39}$N$_{15}$P$_2$Pd (814.1): calcd. C 48.68, N 25.81, H 4.83; found C 48.38, N 24.76, H 4.50. IR (KBr): 2931 (m br), 2230 (w), 1629 (m), 1443 (m), 1384 (m), 1369 (w), 1285 (m), 1245 (m), 1101 (m), 1013 (s), 975 (s), 945 (s), 800 (m), 741 (m), 580 (m) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 8.18–7.45 (m, 2Ph + PhCN, 15H), 4.48 H^A and 4.40 H^B (J_{AB} = 15.0 Hz, NCH^{A}H^{B}N, 12H), 4.20 (s, PCH$_2$N, 12H). ^{13}C{^{1}H} NMR (CDCl$_3$,): δ 165.0 (s, N$_4$C), 126.4–135.0 (C$_{aromatic}$), 73.1 (s, N–CH$_2$–N, PTA), 50.9 (br s, P–CH$_2$–N, PTA). ^{31}P{^{1}H} NMR (CDCl$_3$): δ −47.3 (s).

*4.2.15. Trans-[Pd(N$_4$C(n-NC$_5$H$_4$))$_2$(PTA)$_2$], (**5b**) (n = 2), (**5c**) (n = 3) and (**5d**) (n = 4)*

A mixture of [Pd(N$_3$)$_2$(PTA)$_2$]·CH$_2$Cl$_2$ (**4**·CH$_2$Cl$_2$) (59.0 mg, 0.10 mmol) and n-cyanopyridine (104 mg, 1.0 mmol) in DMF (5 mL) was added to a cylindrical Pyrex tube which was then placed in the focused microwave reactor. The system was left under irradiation for 1 h at 125 °C (the same products were obtained when the mixture of reagents in DMF was refluxed for 12 h). After reaction, the solvent was removed *in vacuo* and the resulting residue was washed repeatedly with 10 mL portions of ethanol and diethyl ether giving yellow microcrystals of *trans*-[Pd(N$_4$C(n-NC$_5$H$_4$))$_2$(PTA)$_2$]. Yield: (**5b**) 55% (39 mg), (**5c**) 50% (36 mg) and (**5d**) 52% (37 mg). Complexes **5b**–**5d** are insoluble in common organic solvents and water. *Trans*-[Pd(N$_4$C(n-NC$_5$H$_4$))$_2$(PTA)$_2$], C$_{24}$H$_{32}$N$_{16}$P$_2$Pd (713.0): calcd. C 40.43, N 31.43, H 4.52; found: (**5b**), C 40.50, N 30.11, H 4.50; (**5c**), C 40.98, N 32.00, H 4.48; (**5d**), C 40.40, N 31.00, H 4.50.

IR (KBr) (**5b**): 2933 (m br), 1671 (m), 1619 (m), 1449 (m), 1421 (m), 1284 (m), 1168 (m), 1010 (s), 974 (s), 945 (s), 808 (m), 580 (m) cm^{-1}; (**5c**): 2933 (m br), 1634 (m), 1423 (m), 1284 (m), 1241 (m), 1097 (m), 1011 (s), 974 (s), 945 (s), 807 (m), 580 (m) cm^{-1}; (**5d**): 2936 (m br), 1671 (w), 1622 (m), 1446 (m), 1420 (m), 1283 (m), 1242 (m), 1097 (m), 1036 (m), 1011 (s), 973 (s), 944 (s), 803 (m), 700 (m), 580 (m) cm^{-1}.

*4.2.16. Liberation of 5-phenyl-1H-tetrazole from **5a***

A yellow suspension of *trans*-[Pd(N$_4$CPh)$_2$(PTA)$_2$]·PhCN, (**5a**)·PhCN (40.7 mg, 0.05 mmol), in aqueous 0.5 M HCl (10 mL) was refluxed for 1 h (Scheme 6). The precipitate formed during the reaction was separated by filtration and the white solid was then extracted with chloroform and shown (by IR and NMR spectroscopies) to be the corresponding 5-phenyl-1*H*-tetrazole (yield *ca.* 50%) [17a]. The remaining white-yellow precipitate is completely insoluble in chloroform, and, by IR (KBr) and elemental analysis, was shown to be [PdCl$_2$(PTA-H)$_2$]Cl$_2$ (**6**) (PTA-H = *N*-protonated PTA cation). [PdCl$_2$(PTA-H)$_2$]Cl$_2$, C$_{12}$H$_{26}$Cl$_4$N$_6$P$_2$Pd(564.6): calcd. C 25.53, N 14.89, H 4.64; found C 25.60, N 14.55, H 4.71. IR (KBr): 2925 (m br), 1443 (m), 1418 (m) 1365 (w), 1286 (m), 1241 (m), 1103 (m), 1014 (s), 973 (s), 898 (m), 810 (m), 740 (m), 575 (m) cm^{-1}. Its insolubility in the common solvents precluded direct NMR analysis, but, upon addition of a diluted NaOH solution in D$_2$O to solid **6** in an NMR tube, the ^{31}P{^{1}H} NMR spectrum exhibits the expected signal of the known deprotonated complex [PdCl$_2$(PTA)$_2$] [28]. Additionally, the ESI$^+$-MS spectrum showed the expected isotopic pattern centred at *m/z* 491 ([M + 1]$^+$), thus confirming the formation of [PdCl$_2$(PTA)$_2$] upon neutralization of **6**.

4.2.17. 5-phenyl-1H-tetrazole

Yield: 80%. IR (cm^{-1}): IR (cm^{-1}): 1636 (C=N). ^{1}H NMR (CDCl$_3$), δ 7.43–8.16 (m, 5H, aromatic). ^{13}C{^{1}H} NMR (CDCl$_3$), δ 126.34–133.93 (C$_{aromatic}$), 158.49 (C=N). ESI$^-$-MS, *m/z* 145 [M − H]$^-$.

4.3. Crystal structure determination

Single crystals of **3b** suitable for X-ray analysis were obtained by slow evaporation of a chloroform solution at room temperature. Intensity data were collected using a Bruker AXS-KAPPA APEX II diffractometer using graphite monochromated Mo-Kα 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 [29]. Structures were solved by direct methods by using the SHELXS–97 package [30] and refined with SHELXL–97 [30]. Calculations were performed with the WinGX System-Version 1.80.03 [31]. All hydrogens were inserted in calculated positions. Least square refinement with anisotropic thermal motion parameters for all the non–hydrogen atoms and isotropic for the remaining were employed. Crystal data and details of data collection for **3b** are given in Table 1.

Acknowledgement

This work has been partially supported by the Fundação para a Ciência e a Tecnologia (FCT), Portugal, and its Strategy Programme PEst-OE/QUI/UI0100/2011 (FEDER funded) as well as by the KBN program (Grant No. N204 280438), Poland. J. L. and M. N. K. express gratitude to the FCT and the Instituto Superior Técnico (IST) for their research contracts (Ciência 2007 program). M. J. F. R. is grateful to the Ministerio de Educación y Ciencia (Spain) for a predoctoral fellowship. The authors gratefully acknowledge Dr. Maria Cândida Vaz (IST) and Dr. Conceição Oliveira for the direction of the elemental analysis and ESI-MS services, respectively, and the Portuguese NMR Network (IST-UTL Centre) for providing access to the NMR facility.

References

[1] R.N. Butler, in: A.R. Katritzky, C.W. Rees, E.F.V. Scriven (Eds.), Comprehensive Heterocyclic Chemistry, vol. 4, Pergamon, Oxford, UK, 1996.
[2] (a) L. Carlucci, G. Ciani, D.M. Proserpio, Angew. Chem. Int. Ed. 38 (1999) 3488;
(b) V.A. Ostrovskii, M.S. Pevzner, T.P. Kofmna, M.B. Shcherbinin, I.V. Tselinskii, Targets Heterocycl. Syst. 3 (1999) 467;
(c) C. Janiak, T.G. Scharmann, W. Gunter, F. Girgsdies, H. Hemling, W. Hinrichs, D. Lentz, Chem. Eur. J. 1 (1995) 637;
(d) C. Janiak, J. Chem. Soc. Chem. Commun. (1994) 545;
(e) G.B. Ansell, J. Chem. Soc. Dalton Trans. (1973) 371.
[3] (a) S. Bhandari, M.F. Mahon, J.G. McGinley, K.C. Molloy, C.E.E. Roper, J. Chem. Soc. Dalton Trans. (1998) 3425;
(b) M. Hill, M.F. Mahon, K.C. Molloy, J. Chem. Soc. Dalton Trans. (1996) 1857;
(c) S. Bhandari, M.F. Mahon, K.C. Molloy, J.S. Palmer, S.F. Sayers, J. Chem. Soc. Dalton Trans. (2000) 1053;
(d) S. Bhandari, C.G. Frost, C.E. Hague, M.F. Mahon, K.C. Molloy, J. Chem. Soc. Dalton Trans. (2000) 663.
[4] (a) L.-Z. Wang, Z.-R. Qu, H. Zhao, X.-S. Wang, R.-G. Xiong, Z.-L. Xue, Inorg. Chem. 42 (2003) 3969;
(b) R.-G. Xiong, X. Xue, H. Zhao, X.-Z. You, B.F. Abrahams, Z. Xue, Angew. Chem. Int. Ed. 41 (2002) 3800;
(c) X. Xue, X.-S. Wang, L.Z. Wang, R.-G. Xiong, B.F. Abrahams, X.-Z. You, Z. Xue, C.-M. Che, Inorg. Chem. 41 (2002) 6544;
(d) J. Tao, Z.-J. Ma, R.-B. Huang, L.-S. Zheng, Inorg. Chem. 43 (2004) 6133.
[5] (a) W.R. Carpenter, J. Org. Chem. 27 (1962) 2085;
(b) H. Quast, L. Bieber, Tetrahedron Lett. 18 (1976) 1485.

[6] (a) Z.P. Demko, K.B. Sharpless, Org. Lett. 3 (2001) 4091;
(b) T.C. Porter, R.K. Smalley, M. Teguiche, B. Purwono, Synthesis 7 (1997) 773;
(c) B. Davis, T. Brandstetter, C. Smith, L. Hackett, B.G. Winchester, G. Fleet, Tetrahedron Lett. 36 (1995) 7507;
(d) L. Garanti, G. Zecchi, J. Org. Chem. 45 (1980) 4767;
(e) R. Fusco, L. Garanti, G. Zecchi, J. Org. Chem. 40 (1975) 1906;
(f) P.A.S. Smith, J.M. Clegg, J.H. Hall, J. Org. Chem. 23 (1958) 524.
[7] (a) D.P. Curran, S. Hadida, S.-Y. Kim, Tetrahedron 55 (1999) 8997;
(b) S.J. Wittenberger, B.G. Donner, J. Org. Chem. 58 (1993) 4139.
[8] (a) A. Kumar, R. Narayanan, H. Shechter, J. Org. Chem. 61 (1996) 4462;
(b) B.E. Huff, M.A. Staszak, Tetrahedron Lett. 34 (1993) 8011.
[9] (a) K. Koguro, T. Oga, S. Mitsui, R. Orita, Synthesis (1998) 910;
(b) W.G. Finnegan, R.A. Henry, R. Lofquist, J. Am. Chem. Soc. 80 (1958) 3908.
[10] (a) Z.P. Demko, K.B. Sharpless, J. Org. Chem. 66 (2001) 7945;
(b) F. Himo, Z.P. Demko, L. Noodleman, K.B. Sharpless, J. Am. Chem. Soc. 125 (2003) 9983.
[11] D. Amantini, R. Beleggia, F. Fringuelli, F. Pizzo, L. Vaccoro, J. Org. Chem. 69 (2004) 2896.
[12] M.L. Kantam, K.B. Shiva Kumar, C. Sridhar, Adv. Synth. Catal. 347 (2005) 1212.
[13] (a) L.V. Myznikov, J. Roh, T.V. Artamonova, A. Hrabalek, G.I. Koldobskii, Russ. J. Org. Chem. 43 (2007) 765;
(b) M. Alterman, A. Hallberg, J. Org. Chem. 65 (2000) 7984.
[14] (a) Z. Ma, J. Tao, R.-B. Huang, L.-S. Zhang, Acta Cryst E61 (2005) m1;
(b) Mitsui Toatsu Chem Inc. (MITK-C) Patent JP 54041878-A (1979).
[15] (a) V.Y. Kukushkin, A.J.L. Pombeiro, Chem. Rev. 102 (2002) 1771;
(b) H.-W. Frühauf, Chem. Rev. 97 (1997) 523;
(c) R.A. Michelin, M. Mozzon, R. Bertani, Coord. Chem. Rev. 147 (1996) 299.
[16] (a) Y.-J. Kim, Y.-S. Kwak, Y.-S. Joo, S.-W. Lee, Dalton Trans. (2002) 144;
(b) Y.-J. Kim, J.-T. Han, S. Kang, W.S. Han, S.-W. Lee, Dalton Trans. (2003) 3357.
[17] (a) P. Smoleński, S. Mukhopadhyay, M.F.C. Guedes da Silva, M.A. Januário Charmier, A.J.L. Pombeiro, Dalton Trans. (2008) 6546;
(b) S. Mukhopadhyay, J. Lasri, M.F.C. Guedes da Silva, M.A. Januário Charmier, A.J.L. Pombeiro, Polyhedron 27 (2008) 2883;
(c) S. Mukhopadhyay, J. Lasri, M.A. Januário Charmier, M.F.C. Guedes da Silva, A.J.L. Pombeiro, Dalton Trans. (2007) 5297;
(d) S. Mukhopadhyay, B.G. Mukhopadhyay, M.F.C. Guedes da Silva, J. Lasri, M.A. Januário Charmier, A.J.L. Pombeiro, Inorg. Chem. 47 (2008) 11334.
[18] J. Lasri, M.F.C. Guedes da Silva, M.N. Kopylovich, B.G. Mukhopadhyay, A.J.L. Pombeiro, Eur. J. Inorg. Chem. (2009) 5541.
[19] (a) T. Li, J.J. García, W.W. Brennessel, W.D. Jones, Organometallics 29 (2010) 2430;
(b) D.-G. Yu, M. Yu, B.-T. Guan, B.-J. Li, Y. Zheng, Z.-H. Wu, Z.-J. Shi, Org. Lett. 11 (2009) 3374;
(c) T.A. Atesin, T. Li, S. Lachaize, W.W. Brennessel, J.J. Garcia, W.D. Jones, J. Am. Chem. Soc. 129 (2007) 7562;
(d) T. Schaub, C. Döring, U. Radius, Dalton Trans. (2007) 1993;
(e) J.J. Garcia, N.M. Brunkan, W.D. Jones, J. Am. Chem. Soc. 124 (2002) 9547;
(f) G.W. Parshall, J. Am. Chem. Soc. 96 (1974) 2360.
[20] M.E. Evans, T. Li, W.D. Jones, J. Am. Chem. Soc. 132 (2010) 16278.
[21] P. Kreutzer, C. Weis, H. Boehme, W. Beck, T. Kemmeric, Z. Natur. B. 27 (1972) 745.
[22] G.B. Ansell, J. Chem. Soc. Dalton Trans. (1973) 371.
[23] (a) J. Bravo, S. Bolãno, L. Gonsalvi, M. Peruzzini, Coord. Chem. Rev. 254 (2010) 555;
(b) A.D. Phillips, L. Gonsalvi, A. Romerosa, F. Vizza, M. Peruzzini, Coord. Chem. Rev. 248 (2004) 955;
(c) S. Chatterjee, I. Biondi, P.J. Dyson, A. Bhattacharyya, Biol. Inorg. Chem. 16 (2011) 715;
(d) W.H. Ang, A. Casini, G. Sava, P.J. Dyson, J. Organometal. Chem. 696 (2011) 989;
(e) E. Vergara, E. Cerrada, A. Casini, O. Zava, M. Laguna, P.J. Dyson, Organometallics 29 (2010) 2596;
(f) A. Mena-Cruz, P. Lorenzo-Luis, V. Passarelli, A. Romerosa, M. Serrano-Ruiz, Dalton Trans. 40 (2011) 3237;
(g) A. Lis, M.F.C. Guedes da Silva, A.M. Kirillov, P. Smoleński, A.J.L. Pombeiro, Cryst. Growth Des 10 (2010) 5245.
[24] (a) A. Loupy (Ed.), Microwaves in Organic Synthesis, Wiley/VCH, Weinheim, 2002;
(b) J.P. Tierney, P. Lidström (Eds.), Microwave Assisted Organic Synthesis, Blackwell Publishing/CRC Press, Oxford, 2005.
[25] W.P. Fehlhammer, T. Kemmerich, W. Beck, Chem. Ber 116 (1983) 2691.
[26] R.A. Michelin, G. Facchin, P. Uguagliati, Inorg. Chem. 23 (1984) 961.
[27] (a) D.J. Daigle, A.B. Pepperman Jr., S.L. Vail, J. Heterocycl. Chem. 11 (1974) 407;
(b) D.J. Daigle, Inorg. Synth. 32 (1998) 40.
[28] D.J. Darensbourg, T.J. Decuir, N.W. Stafford, J.B. Robertson, J.D. Draper, J.H. Reibenspies, Inorg. Chem. 36 (1997) 4218.
[29] G.M. Sheldrick, Acta Crystallogr. Sect. A 46 (1990) 467.
[30] G.M. Sheldrick, SHELXL-97. University of Gottingen, Germany, 1997.
[31] L.J. Farrugia, J. Appl. Crystallogr. 32 (1999) 837.