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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

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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$_4$CR)$_2$(PPh$_3$)$_2$] (**3**) [R = Me (**3a**), Ph (**3b**), 4-ClC$_6$H$_4$ (**3c**), 4-FC$_6$H$_4$ (**3d**), 2-NC$_5$H$_4$ (**3e**), 3-NC$_5$H$_4$ (**3f**), 4-NC$_5$H$_4$ (**3g**)]. The reaction of *trans*-[Pd(N$_3$)$_2$(PPh$_3$)$_2$] (**1**) with propionitrile (**2h**) also affords, apart from *trans*-[Pd(N$_4$CEt)$_2$(PPh$_3$)$_2$] (**3h**), the unexpected mixed cyano-tetrazolato complex *trans*-[Pd(CN)(N$_4$CEt)(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$_4$CR)$_2$(PTA)$_2$] (**5**) [R = Ph (**5a**), 2-NC$_5$H$_4$ (**5b**), 3-NC$_5$H$_4$ (**5c**), 4-NC$_5$H$_4$ (**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$_4$CPh)$_2$(PTA)$_2$] (**5a**) was achieved. The complexes were characterized by IR, ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} 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*-

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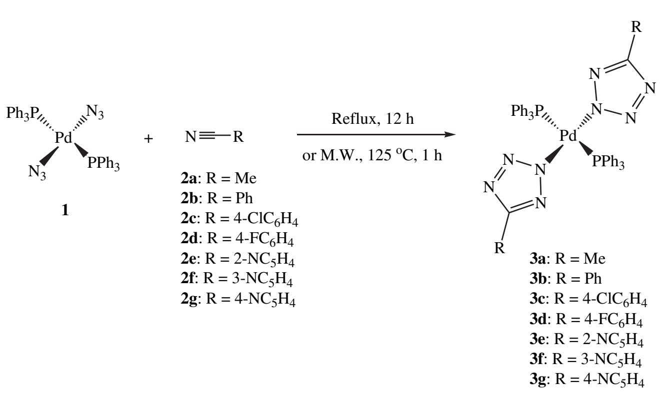
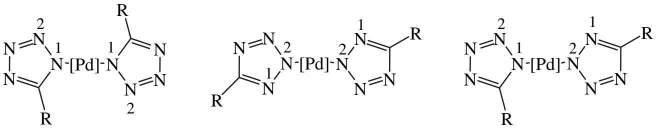
$[Pt(N_3)_2(PPh_3)_2]$ can react with nitriles NCR to give the bis(tetrazolato) compounds *trans*-$[Pt(N_4CR)_2(PPh_3)_2]$ from which the tetrazoles can be liberated. Very recently, we have reported that [2 + 3] cycloaddition of *cis*-$[Pt(N_3)_2(PPh_3)_2]$ with 4-cyanobenzaldehyde furnishes a (formylphenyl)tetrazolate 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.



(a) N^1N^1-coordination (b) N^2N^2-coordination (c) N^1N^2-coordination

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

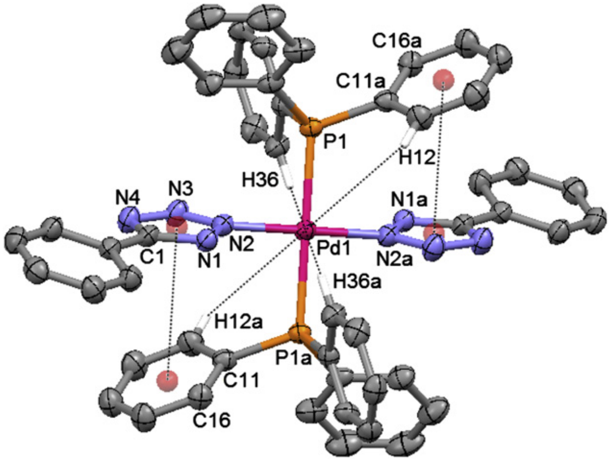


Fig. 1. Thermal ellipsoid plot, drawn at the 50% probability level, of the *trans* 5-phenyltetrazolato palladium(II) complex **3b** with atomic numbering scheme. Selected bond lengths (Å) and angles (°): Pd1–P1 2.3469(4), Pd1–N2 1.9953(15), P1–Pd1–N2 91.49(4), N2–Pd1–P1a 88.50(4). $\pi\cdots\pi$ and agostic interactions (shown as dashed lines): *centroid⋯centroid* 3.6536(12) Å; $d(H12\cdots Pd1)$ 3.40 Å, $\angle(C12-H12\cdots Pd1)$ 107.09°; $d(H36\cdots Pd1)$ 2.93 Å, $\angle(C36-H36\cdots Pd1)$ 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.