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Activation of C–CN bond of propionitrile: An alternative route to the syntheses of 5-substituted-1*H*-tetrazoles and dicyano-platinum(II) species

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ABSTRACT

Reaction of *trans*-$[Pt(N_4CR)_2(PPh_3)_2]$ **1** (R = Me **1a**, Et **1b**, Ph **1c**, CH_2CH_2Ph **1d**) with propionitrile under reflux gives *trans*-$[Pt(CN)_2(PPh_3)_2]$ **2** along with 5-substitued-1*H*-tetrazoles N_4CR **3** (R = Me **3a**, Et **3b**, Ph **3c**, CH_2CH_2Ph **3d**) in moderated to good yield, respectively. Treatment of *cis*-$[Pt(N_3)_2(PPh_3)_2]$ **5** with alkynes HC≡CR′ **6** (R′ = Ph **6a**, *p*-MeC_6H_4 **6b**) under focused microwave irradiation leads, upon azide replacement, to the formation of the dialkynyl complexes *trans*-$[Pt(C{\equiv}CR')_2(PPh_3)_2]$ **7** (R′ = Ph **7a**, *p*-MeC_6H_4 **7b**) which also furnish the dicyano-platinum complex **2** in refluxing propionitrile. In both cases, the reactions leading to the formation of **2** proceed *via* an unusual oxidative addition, involving NC–C bond cleavage of two propionitrile molecules, and a reductive elimination process.

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1. Introduction

Tetrazoles constitute an important class of compounds with applications in areas of medicinal chemistry [1] and material science [2], and are precursors for nitrogen-containing heterocycles [3]. In 1958, Finnegan et al. [4] published the synthesis of 5-substituted tetrazoles by heating nitriles and sodium azide in DMF. Later on several synthetic methods based on [2+3] cycloaddition of organonitriles and azides have been reported, by using tin or silicon azides [5], a strong Lewis acid [6] or a strong acidic media [4,7]. Sharpless and Demko [8] improved the method by using a zinc salt as the Lewis acid and performing the reactions in aqueous media. Pizzo and coworkers [9] efficiently synthesized tetrazoles by the addition of trimethylsilyl azide to organic nitriles using tetrabutylammonium fluoride as catalyst. The use of nanomaterials as catalysts [10] and microwave irradiation [11] to shorten the reaction time has been also reported by different authors. Moreover, we have recently reported [12] the formation of 5-ethyl-1*H*-tetrazole by refluxing *cis*-$[Pt(N_3)_2(PPh_3)_2]$ or the tetrazolato complex *trans*-$[Pt(N_4CEt)_2(PPh_3)_2]$ in propionitrile. To explore the scope and generality of this method to the synthesis of 5-R-1*H* tetrazoles, where R is an alkyl or aryl group, we have now studied the reaction of propionitrile with a series of tetrazolato *trans*-$[Pt(N_4CR)_2(PPh_3)_2]$ complexes and herein we report this generalized and easy pathway for obtaining such substituted tetrazoles in good yields. They were isolated upon liberation of the corresponding tetrazolato ligands from the precursor platinum complexes on treatment with propionitrile.

On the other hand it has been found that cyanide is among the few ligands with the capability to stabilize both low- and high-valent transition metal complexes, and its high electronic and coordinative versatility has allowed the formation of a variety of cyano complexes [13]. Unfortunately, the synthesis of cyano-transition metal complexes usually involves hazardous chemicals such as an alkali metal cyanide. A limited number of other sources of cyano-ligands are known but usually they concern only specific cases. Among them, formaldoxime [14], diaminomaleonitrile [15] and diiminosuccinonitrile [16] were used to synthesize some copper and cobalt cyano-complexes, while trimethylsilyl cyanide ($NCSiMe_3$) was applied to the preparation of cyano- and isocyano-complexes of rhenium [17] and iron [17a,18]. The cyano ligand can also be obtained by deprotonation of ligated isocyanide CNH and aminocarbyne CNH_2 [17a,17b,17c,17e,18]. Oxidative addition of an organonitrile or ethylcyanoformate at a zero-valent group 10 transition metal has been also reported to produce a cyano-complex of the corresponding metal ion [19]. In the current work we have achieved the synthesis of *trans*-$[Pt(CN)_2(PPh_3)_2]$ starting from bis(tetrazolato) or bis(alkynyl) platinum(II) complexes where the solvent propionitrile acts as the precursor of the cyano-ligands.

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2. Experimental

2.1. General and physical measurements

Solvents were purchased from Aldrich and dried by usual procedures. *Trans*-[Pt(N_4CR)$_2$(PPh_3)$_2$] **1** [R = Me **1a**, Et **1b**, Ph **1c**], *trans*-[Pt(CN)(N_4CEt)(PPh_3)$_2$] **4** and *cis*-[Pt(N_3)$_2$(PPh_3)$_2$] **5** were prepared according to published procedures [12,20]. C, H and N elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. ^{1}H, ^{13}C and ^{31}P{^{1}H} NMR spectra (in $CDCl_3$) were measured on a Varian Unity 300 spectrometer at ambient temperature. The chemical shifts (δ) are expressed in ppm relative to Si(Me)$_4$ (^{1}H and ^{13}C) or 85% H_3PO_4 (^{31}P). *J* values are in Hertz. Infrared spectra (4000–400 cm^{-1}) were recorded on a Bio-Rad FTS 3000MX and a Jasco FT/IR-430 instruments in KBr pellets and the wavenumbers are in cm^{-1}.

Electrospray mass spectra of 5-substituted-1*H*-tetrazoles 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 CH_2Cl_2) 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* = 50–1500. The compounds were observed in the negative mode (capillary voltage = −4000 V). 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.

2.2. Compounds preparation

2.2.1. *trans*-[Pt(5-phenethyltetrazolato)$_2$(PPh_3)$_2$] (**1d**)

(i) By refluxing: A solution of *cis*-[Pt(N_3)$_2$(PPh_3)$_2$] **5** (0.080 g, 0.10 mmol) in $NCCH_2CH_2Ph$ (8 mL) was refluxed for 12 h whereupon the solvent was removed *in vacuo*. The oily residue was treated with diethyl ether to obtain, upon stirring, a white semicrystalline solid. This was washed repeatedly with 5 mL portions of water, and then with ethanol and lastly with diethyl ether. Recrystallization from a chloroform/diethyl ether mixture gave off-white crystals of *trans*-[Pt(5-phenethyltetrazolato)$_2$(PPh_3)$_2$] **1d**.

(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 100 °C. The solvent was then removed *in vacuo* and the resulting oily residue was treated in a manner similar to that described above to obtain a white crystalline solid of **1d**. Yield: 52% (method i) and 50% (method ii). IR (cm^{-1}): 1629 (C=N). ^{1}H NMR ($CDCl_3$), δ 2.51 (m, 8H, CH_2), 7.11–7.51 (m, 40H, aromatic). ^{13}C{^{1}H} NMR ($CDCl_3$), δ 27.19 (CH_2), 34.47 (CH_2), 125.84–141.79 ($C_{aromatic}$), 164.46 (C=N). ^{31}P{^{1}H} NMR ($CDCl_3$), δ 16.51 (J_{Pt-P} = 2726 Hz). *Anal.* Calc. for $PtC_{54}H_{48}N_8P_2$: C, 60.79; H, 4.50; N, 10.50. Found: C, 60.49; H, 4.30; N, 10.39%.

2.2.2. *trans*-[Pt(C≡CPh)$_2$(PPh_3)$_2$] (**7a**)

A solution of *cis*-[Pt(N_3)$_2$(PPh_3)$_2$] **5** (0.080 g, 0.10 mmol) in ethynylbenzene (3 mL) was taken in a cylindrical Pyrex tube which was then placed in the focused microwave reactor. The system was irradiated for 1 h at 100 °C. Then the mixture was cooled and excess of diethyl ether was added to precipitate a yellow compound which was isolated by filtration and washed with diethyl ether and dried at room temperature. The resultant compound **7a** was recrystallized from a dichloromethane and diethyl ether solvent mixture. Yield: 65%. IR (cm^{-1}): 2109 (C≡C). ^{1}H NMR ($CDCl_3$), δ 6.27–6.92 (m, 10H, C_6H_5), 7.33–7.86 (m, 30H, P(C_6H_5)). ^{31}P{^{1}H} NMR ($CDCl_3$), δ 18.60 (J_{Pt-P} = 2650 Hz). *Anal.* Calc. for $PtC_{52}H_{40}P_2$: C, 67.75; H, 4.37. Found: C, 67.32; H, 4.46%. Due to poor solubility no reliable results were obtained for ^{13}C NMR spectroscopy.

2.2.3. *trans*-[Pt(*p*-MeC_6H_4C≡C)$_2$(PPh_3)$_2$] (**7b**)

This compound was prepared by a similar method to that used for **7a**, but by using 1-ethynyl-4-methylbenzene as the solvent. Yield: 62%. IR (cm^{-1}): 2105 (C≡C). ^{1}H NMR ($CDCl_3$), δ 2.16 (s, 6H, CH_3), 6.16–6.73 (m, 8H, C_6H_4), 7.34–7.82 (m, 30H, P(C_6H_5)). ^{31}P{^{1}H} NMR ($CDCl_3$), δ 18.55 (J_{Pt-P} = 2655 Hz). *Anal.* Calc. for $PtC_{54}H_{44}P_2$: C, 68.27; H, 4.67. Found: C, 67.98; H, 4.82%. Due to poor solubility no reliable results were obtained for ^{13}C NMR spectroscopy.

2.2.4. *trans*-dicyano bis(triphenylphosphine)platinum(II) complex 2 and 5-substituted-1H-tetrazoles

This compound was prepared in identical ways starting from **1a**, **1c**, **1d**, **7a** or **7b** by refluxing any of these complexes in propionitrile for 24 h. The following synthesis is described as a representative case.

A solution of *trans*-[Pt(N_4CCH_3)$_2$ (PPh_3)$_2$] **1a** (0.088 g, 0.10 mmol) in NCEt (8 mL) was refluxed for 24 h whereupon the solvent was removed to half of its volume *in vacuo*. The reaction mixture was left to cool to room temperature and was treated with diethyl ether (5 mL). The white solid **2** was isolated by filtration and washed with diethyl ether for several times and chromatographic purification of the complex on SiO_2 was carried out using dichloromethane/diethyl ether (10:1). The mother liquor was evaporated to dryness and the resulting compound was identified as 5-methyl-1*H*-tetrazole.

A slight modification was followed when starting from *trans*-[Pt(5-ethyltetrazolato)$_2$(PPh_3)$_2$] **1b**. When refluxing its solution in propionitrile, the intermediate complex *trans*-[Pt(CN)(5-ethyltetrazolato)(PPh_3)$_2$] **4** started to precipitate after 6 h, whereupon 5 mL of DMF (dimethylformamide) was added to solubilize the complex, thus allowing the reaction to proceed further.

2.2.5. *trans*-[Pt(CN)$_2$(PPh_3)$_2$] (**2**)

Yield: 60%. IR (cm^{-1}): 2129 (C≡N). ^{1}H NMR ($CDCl_3$), δ 7.43–7.72 (m, 30H, aromatic). ^{13}C{^{1}H} NMR ($CDCl_3$), δ 125.70 (C≡N), 128.49–141.08 ($C_{aromatic}$). ^{31}P{^{1}H} NMR ($CDCl_3$), δ 14.42 (J_{Pt-P} = 2377 Hz). *Anal.* Calc. for $PtC_{38}H_{30}N_2P_2$: C, 59.14; H, 3.92; N, 3.63. Found: C, 59.13; H, 3.90; N, 3.25%.

2.2.6. 5-Methyl-1H-tetrazole (**3a**)

Yield: 70%. IR (cm^{-1}): 1629 (C=N). ^{1}H NMR ($CDCl_3$), δ 2.60 (s, 3H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$), δ 9.18 (CH_3), 153.21 (C=N). ESI-MS, *m/z* 83 [M−H]$^-$.

2.2.7. 5-Ethyl-1H-tetrazole (**3b**)

Yield: 75%. All the spectroscopic and ESI-MS data are in agreement with those reported earlier [18].

2.2.8. 5-Phenyl-1H-tetrazole (**3c**)

Yield: 80%. 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]$^-$.

2.2.9. 5-Phenethyl-1H-tetrazole (**3d**)

Yield: 77%. IR (cm^{-1}): 1634 (C=N). ^{1}H NMR ($CDCl_3$), δ 3.09 (t, J_{HH} = 9 Hz, 2H, CH_2), 3.24 (t, J_{HH} = 9 Hz, 2H, CH_2), 7.12–7.54 (m, 5H, aromatic). ^{13}C{^{1}H} NMR ($CDCl_3$), δ 25.40 (CH_2), 33.64 (CH_2), 126.58–139.61 ($C_{aromatic}$), 155.94 (C=N). ESI-MS, *m/z* 173 [M−H]$^-$.

Table 1
Summary of crystal data, data collection and structure refinement for the X-ray diffraction study of complexes **2** and **7a**

	2	**7a**
Empirical formula	$C_{38}H_{30}N_2P_2Pt$	$C_{52}H_{40}P_2Pt$
Formula weight	771.66	921.86
Crystal system	triclinic	orthorhombic
Space group	$P\bar{1}$	Pbca
a (Å)	9.1519(20)	18.051(2)
b (Å)	9.6660(26)	9.5650(11)
c (Å)	10.3888(22)	22.929(2)
α (°)	109.959(13)	90
β (°)	90.901(14)	90
γ (°)	108.283(16)	90
V (Å^3)	812.4(4)	3958.9(8)
Z	1	4
ρ (g cm^{-3})	1.577	1.547
μ(Mo Kα)	4.445	3.662
Number of reflections measured	7409	28382
Number of reflections unique	2805	8069
Number of reflections observed	2802	4091
R_{int}	0.0339	0.0410
R_1, wR_2 (all data)	0.0243, 0.0572	0.0797, 0.0611
R_1, wR_2 (obs. refl.)	0.0242, 0.0572	0.0262, 0.0476
Goodness-of-fit	1.034	0.913

2.3. Single-crystal X-ray crystallography

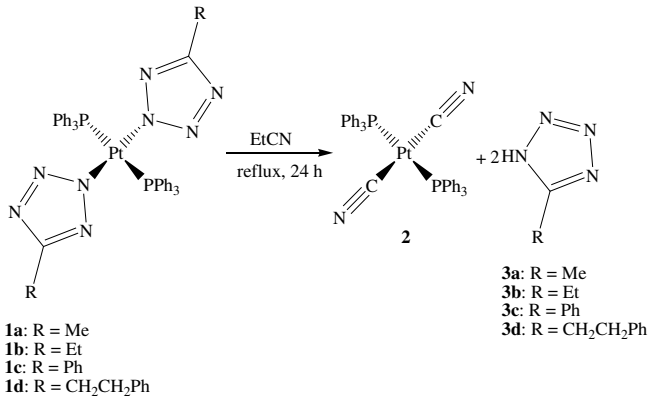
Single crystals of **2** were obtained by diffusing diethyl ether in dichloromethane solutions of the complex. X-ray diffraction suitable crystals of **7a** were obtained by slow evaporation of the reaction mixture.

X-ray intensity data were measured at 150 K on a Bruker AXS-KAPPA APEX II CCD-based diffractometer (Mo Kα radiation, λ = 0.71073 Å) using omega scans of 0.5° per frame, and a full sphere of data was obtained. Raw data frame integration and corrections were performed with Bruker SAINT. An empirical absorption correction was applied with SADABS. Direct methods structure solution were performed with SHELXS-97 package [21] and refined with SHELXL-97 [22] with the WinGX graphical user interface [23]. 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 atoms were employed. Crystallographic parameters and residuals are given in Table 1.

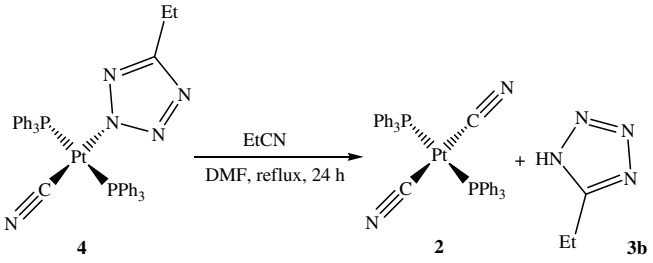
3. Results and discussion

The phenethyltetrazolato complex *trans*-[Pt(N$_4$CR)$_2$(PPh$_3$)$_2$] **1d** (R = CH$_2$CH$_2$Ph) was prepared by using either the traditional refluxing method or by microwave irradiation (M.W.) as reported in a previous paper for the synthesis of the analogous complexes **1a** (R = Me), **1b** (R = Et) and **1c** (R = Ph) [12]. Treatment of any of these complexes with an excess of propionitrile in refluxing conditions leads ultimately to the dicyano-Pt^{II} compound *trans*-[Pt(CN)$_2$(PPh$_3$)$_2$] **2**, isolated as a white crystalline solid in moderate yield (*ca.* 60%), with concomitant formation of the corresponding 5-substituted-1*H*-tetrazoles **3** in good yields (*ca.* 80%) (Scheme 1).

The dicyano-complex **2** was synthesized and reported for the first time by Bailar et al. [24], using [PtCl$_2$(PPh$_3$)$_2$] and KCN as the source of the cyano-ligand. When starting from *trans*-[Pt(N$_4$CEt)$_2$(PPh$_3$)$_2$] **1b**, the addition of a small amount of DMF is required to prevent the precipitation of the intermediate mono-cyano complex *trans*-[Pt(CN)(N$_4$CEt)(PPh$_3$)$_2$] **4**. This intermediate has been isolated by a method described elsewhere [12] and converts to *trans*-[Pt(CN)$_2$(PPh$_3$)$_2$] **2** by dissolving in DMF and then refluxing a propionitrile solution for 24 h (Scheme 2).



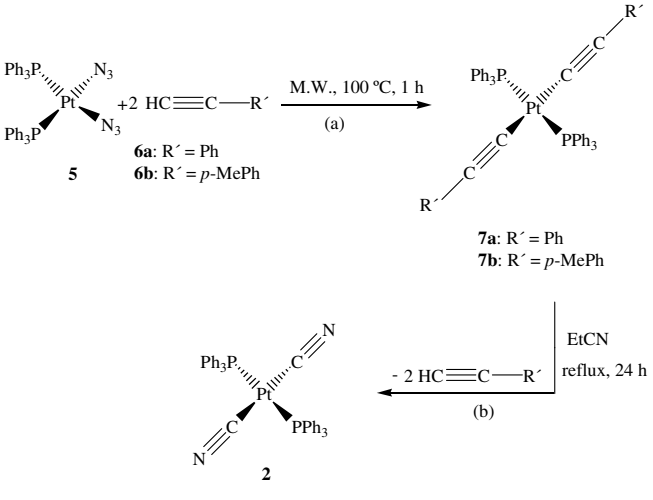
Scheme 1.



Scheme 2.

In all the above cases the dicyano-complex **2** precipitates on addition of diethyl ether and is further purified chromatographically using dichloromethane/diethyl ether as eluent. Evaporation of the mother liquor provides the respective 5-substitued-1*H*-tetrazole **3** (Scheme 1) as an off-white solid.

The dialkynyl complexes *trans*-[Pt(C≡CR′)$_2$(PPh$_3$)$_2$] **7** (R′ = Ph **7a**, *p*-MeC$_6$H$_4$ **7b**), analogous to the dicyano compound **2**, were obtained by reaction of *cis*-[Pt(N$_3$)$_2$(PPh$_3$)$_2$] **5** with ethynylbenzene **6a** or 1-ethynyl-4-methylbenzene **6b**, respectively (reaction a, Scheme 3), under focused microwave irradiation (1 h, 100 °C, 300 W). This unexpected overall replacement of the azide ligands by alkynyl groups occurs instead of the anticipated formation of triazolato complexes upon metal-promoted [2+3] cycloaddition

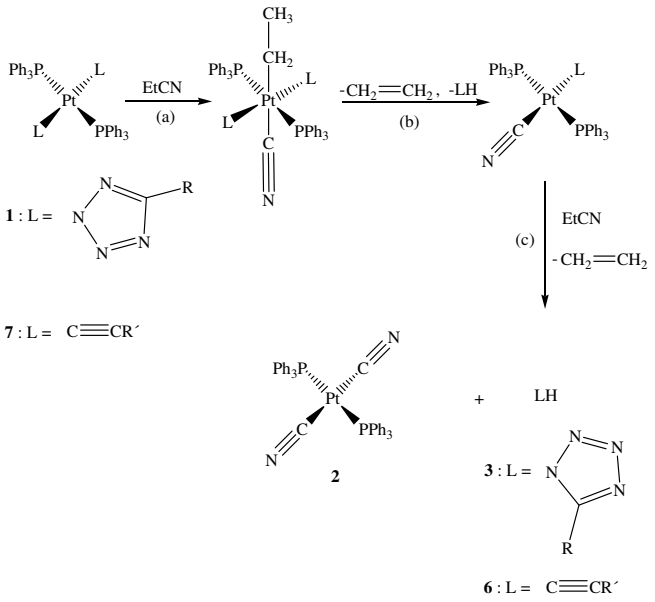


Scheme 3.

between the ligated azides and the alkynes. Complex **7a** was previously synthesized [25] starting from *cis*-$[PtCl_2(PPh_3)_2]$. Both **7a** and **7b** have been characterized by means of IR, ^1H, and $^{31}P\{^1H\}$ NMR spectroscopies, elemental analyses and X-ray crystallographically (for complex **7a**). The observed spectroscopic data are in accordance with those of related alkynyl complexes reported elsewhere [26]. The dialkynyl complexes **7a** and **7b** also furnish the dicyano-platinum complex **2** upon refluxing in propionitrile for 24 h (reaction b, Scheme 3).

The formation of the dicyano-platinum(II) complex **2** is believed to proceed, in all the cases, *via* activation of the C–CN bond in propionitrile. In fact, all the attempts to transform the bis(tetrazolato) complexes **1** or the dialkynyl complexes **7** into **2** in the absence of propionitrile have failed (the starting materials were then recovered quantitatively), namely when a CH_2Cl_2 solution of **1** or **7** was refluxed for 36 h or heated under focused M.W. irradiation (2 h, 100 °C), also in solid phase (SiO_2) without solvent. These results indicate that propionitrile is the precursor of the cyanide ligand in complex **2**.

A possible pathway for the conversion of the bis(tetrazolato) complexes **1** or the dialkynyl compounds **7** into **2** is proposed in Scheme 4. It involves an oxidative addition of propionitrile (which thus undergoes NC–C bond cleavage) to Pt^{II} to give a cyano-ethyl-Pt^{IV} intermediate (reaction a, Scheme 4), followed by β-elimination from the ethyl ligand to form ethylene, and reductive elimination of the corresponding 5-substituted-1*H*-tetrazole **3** or alkyne **6** to yield the mixed cyano-tetrazolato or cyano-alkynyl platinum(II) complex, respectively (reaction b, Scheme 4). In most of the cases the high solubility of these mono-cyano complexes in propionitrile allows the reaction to proceed further towards a second oxidative addition of EtCN and reductive elimination step (reaction c, Scheme 4), ultimately giving the dicyano-complex **2**. The evolution of ethylene gas assists in driving these reactions. Efforts to isolate the intermediate mixed cyano-tetrazolato or cyano-alkynyl complexes failed except in the case of *trans*-$[Pt(N_4CEt)_2(PPh_3)_2]$ **1b** where *trans*-$[Pt(CN)(N_4CEt)(PPh_3)_2]$ **4** precipitates from the reaction mixture due to its poor solubility in propionitrile. Quantitative recovery of complex **1a** or **1c** upon prolonged refluxing in benzonitrile or in acetonitrile, respectively, *i.e.* N≡CR solvents with R groups which can not undergo β-elimination, reinforces the proposed mechanistic pathway.



Scheme 4.

Table 2
Selected bond distances (Å) and angles (°) for complexes **2** and **7a**

	2	7a
Bond lengths		
Pt1–P1	2.3210(12)	2.3118(7)
Pt1–C1	1.987(5)	2.004(3)
N1–C1	1.154(7)	
C1–C2		1.204(4)
Bond angles		
P1–Pt1–C1	88.25(13)	86.68(8)
P1–Pt1–C1[a]	91.75(13)	93.34(8)
Pt1–C1–C2		173.0(2)
Pt1–C1–N1	176.8(4)	

[a] Symmetry operation to generate equivalent atom: $-x, -y, -z$.

The 5-substituted-1*H*-tetrazoles **3** were isolated in good yields (*ca.* 80%) and characterized by IR, ^1H and ^{13}C NMR spectral data and electrospray mass spectrometry (ESI-MS). The ^{13}C NMR resonances of the tetrazole ring carbon atoms *C*=N (153.2–159.9 ppm) are observed at a higher field than those of the corresponding complex precursors **1** (*ca.* 164 ppm).

The obtained complex **2** was characterized by elemental analysis, IR and ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ spectroscopies. The IR band at 2129 cm^{-1} and the ^{13}C resonance at 125.7 ppm confirm the presence of the cyano ligand in the complex [27]. In the $^{31}P\{^1H\}$ NMR spectrum, the $J(^{31}P\text{-}^{195}Pt)$ value of 2726 Hz is typical for the *trans* configuration in solution [28].

The single-crystal X-ray diffraction structural analyses of **2** and **7a** confirm the formulations of the respective complexes. Selected bond lengths and angles and crystallographic data are given in Tables 1 and 2. The crystal structure of *trans*-$[Pt(CN)_2(PPh_3)_2]$ with one methanol molecule as solvent of crystallization was reported previously [29].

In both compounds **2** and **7a**, the metal center is essentially square-planar, the Pt atoms lie on inversion centers and the bulky PPh_3 ligands are mutually *trans* (Figs. 1 and 2). The bond lengths

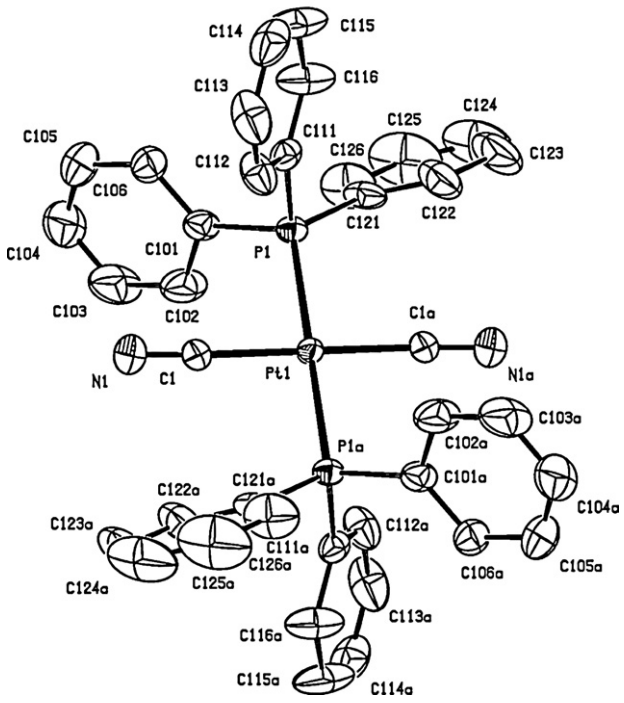


Fig. 1. Molecular structure of *trans*-$[Pt(CN)_2(PPh_3)_2]$ **2** with atomic numbering scheme (ellipsoids are drawn at 50% probability).

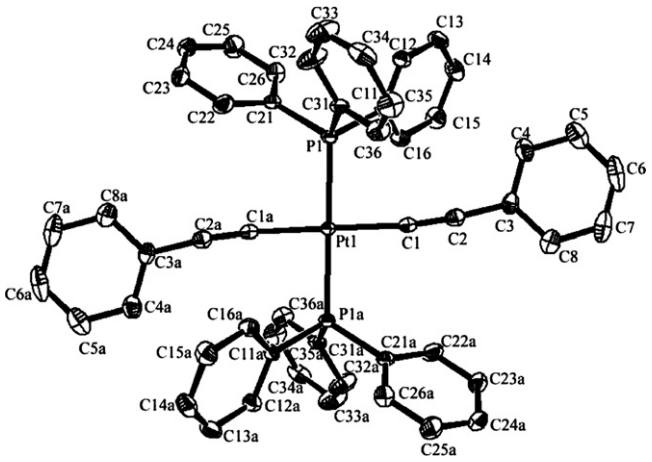


Fig. 2. Molecular structure of *trans*-[Pt(C≡CPh)$_2$(PPh$_3$)$_2$] **7a** with atomic numbering scheme (ellipsoids are drawn at 50% probability).

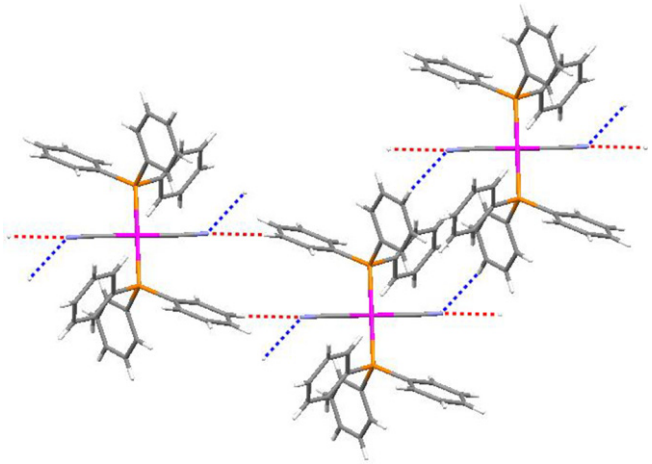


Fig. 3. A three-dimensional sheet of **2**. The C–H···N weak hydrogen bonding interactions that sustain the sheets are shown as dots (blue dots refer to the H114···N1 interaction and the red dots to the H123···N1 interaction). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

between the platinum ion and the donating atoms are within the ranges reported for related Pt(II) complexes [30].

The centrosymmetric molecules of **2** are connected by a set of C–H···N weak hydrogen bonding interactions, which arrange the molecules into three-dimensional sheets (Fig. 3) since the nitrogen N1 lone pair of one molecule is oriented towards the phenyl hydrogen atoms H114 and H123, of two other molecules. The H114···N1 and H123···N1 distances for these interactions are 2.55 Å and 2.74 Å, respectively.

4. Conclusion

In this work, we have shown that both the bis(tetrazolato) and the dialkynyl complexes *trans*-[Pt(N$_4$CR)$_2$(PPh$_3$)$_2$] and *trans*-[Pt(C≡CR′)$_2$(PPh$_3$)$_2$], respectively, react with propionitrile to furnish dicyano-complex *trans*-[Pt(CN)$_2$(PPh$_3$)$_2$] *via* an unusual oxidative addition (involving NC–C bond cleavage of two propionitrile molecules) followed by a reductive elimination process. It also provides an alternative metal-assisted route to prepare 5-substituted-1*H*-tetrazole compounds in an easy and convenient way. The extension of these methods to the preparation of (i) other cyano-complexes, namely of the types [Pt(CN)$_2$L$_2$] and [Pt(CN)$_2$X$_2$L$_2$] (X = single-electron donating ligand, L = two-electron donor ligand), without the need to use toxic chemicals (such as an alkali metal cyanide) and (ii) other 5-substituted tetrazoles (simply by changing the R group of the organonitrile NCR precursors), are worth to be pursued.

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Appendix A. Supplementary data

CCDC 680289 and 680290 contain the supplementary crystallographic data for **7a** and **2**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2008.06.031.

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