

Platinum(II)-Promoted [2+3] Cycloaddition of Azide with 4-Cyanobenzaldehyde, a Schiff Base Derivative or Dicyanobenzenes To Give Formyl-, Amino(imino)- or Cyano-Functionalized Tetrazolato Complexes

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The [2+3] cycloaddition reaction (which is greatly accelerated by microwave irradiation) of the bis(azido)platinum(II) compound *cis*-[Pt(N₃)₂(PPh₃)₂] (**1**) with 4-cyanobenzaldehyde (**2**) furnishes the *N*²*N*²-bonded isomer of bis[5-(4-formylphenyl)tetrazol-2-ate] platinum(II) *trans*-[Pt(N₄CC₆H₄(4-CH=O))₂(PPh₃)₂] (**3a**) as the major product, along with the *N*¹*N*²-bonded isomer **3b**. Treatment of **3a** with 2-dimethylaminoethylamine (**4**), in refluxing methanol, gives the corresponding *N*²*N*²-bonded bis[(*E*)-5-(4-[(2-(dimethylamino)ethylimino)methyl]phenyl)tetrazol-2-ate] platinum(II) complex *trans*-[Pt(N₄CC₆H₄(4-CH=NCH₂CH₂NMe₂))₂(PPh₃)₂] (**6**) in good yield. An alternative route involves the reaction of 4-cyanobenzaldehyde (**2**) with diamine **4** to give the *E* isomer of 4-[(2-(dimethylamino)ethylimino)methyl]benzonitrile N≡CC₆H₄(4-CH=NCH₂CH₂NMe₂) (**5**), followed by the reaction of the latter with bis(azido)platinum(II) complex **1** to afford **6** in similar yield. The reaction of **6** with MCl₂ (M = Pd, Ni, Zn, Cu), at room temperature for 3 h regenerates complex

3a as a result of the Schiff base hydrolysis, along with the diamine complex [MCl₂(NH₂CH₂CH₂NMe₂)] (**7**). Treatment of **6** with ZnCl₂ for 36 h affords a mixture of **3a** with its substitution products [Pt{HN₄CC₆H₄(4-CH=O)}(NH₂CH₂CH₂NMe₂)(PPh₃)]Cl₂ (**9**; isolated in the tetrazole form) and *cis*-[PtCl₂(PPh₃)₂] (**10**) and diamine complex **7** (M = Zn). The [2+3] cycloaddition reactions of *cis*-[Pt(N₃)₂(PPh₃)₂] (**1**) with unsubstituted dicyanobenzenes **11** [1,2-C₆H₄(CN)₂ (**11a**), 1,3-C₆H₄(CN)₂ (**11b**), 1,4-C₆H₄(CN)₂ (**11c**)] occur regioselectively and give the corresponding *N*²*N*²-bonded bis[5-(cyano-phenyl)tetrazol-2-ate] *trans*-[Pt(N₄CC₆H₄R)₂(PPh₃)₂] complexes **12** (R = 2-CN **12a**, 3-CN **12b**, 4-CN **12c**). The isolated compounds were characterized by IR, ¹H NMR, ¹³C NMR and ³¹P{¹H} NMR (metal complexes) spectroscopy, elemental analyses, ESI-MS and X-ray structural analyses (for **3a**, **5**·HCl, **7**, **9** and **12a**).

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Introduction

Tetrazoles have found a wide range of applications in areas as diverse as coordination chemistry, medicinal chemistry and materials science.^[1–4] They can be obtained by [2+3] cycloaddition of an organonitrile with an azide, but only a few activated nitriles are known to undergo this reaction in an *intermolecular* 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 by *intramolecular* [2+3] cyclo-

addition.^[6] The cycloaddition can also be promoted by using fluoros tin or a 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 by performing the reaction in aqueous medium. Amantini et al.^[11] efficiently synthesized tetrazoles by reaction of trimethylsilyl azide with a nitrile by using tetrabutylammonium fluoride as the catalyst. The use of nanocrystalline ZnO as a heterogeneous catalyst^[12] and microwave irradiation^[13] to shorten the reaction time has also been reported. Phthalonitrile and terephthalonitrile react with azides in the presence of a metal chloride as catalyst to give monotetrazoles.^[14] The formation of substituted tetrazoles can be achieved by using a transition-metal-coordinated azide and free organonitriles^[15] or isonitriles.^[16] For example, we recently reported^[17,18] that the diazido complexes *cis*-[Pt(N₃)₂(L)₂] [L = PPh₃ or 1,3,5-triaza-7-phosphaadamantane (PTA)] can be applied as starting materials for the synthesis of 5-substituted tetrazoles upon [2+3] cycloadditions with NCR to give the bis(tetrazolato) complexes *trans*-[Pt(N₄CR)₂(L)₂] from which the tetrazoles can be liberated.

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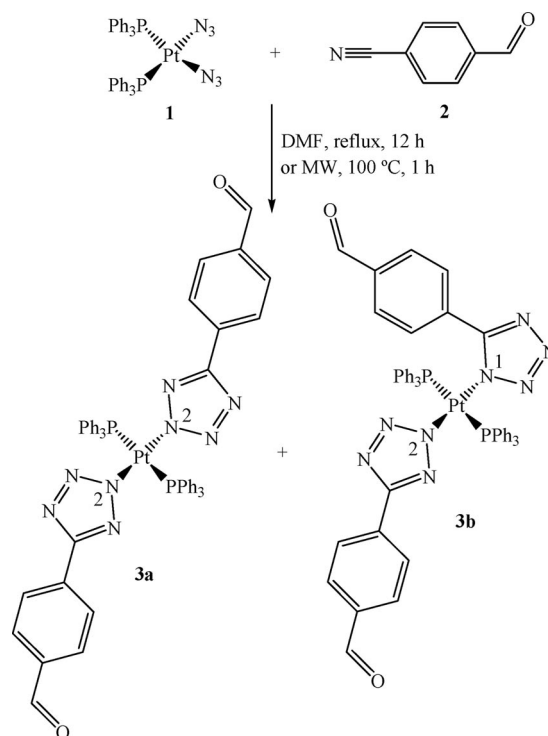
The current work aims to extend the [2+3] cycloaddition of an azide with a nitrile to an easy synthesis of functionalized tetrazolato–Pt complexes in which the tetrazolato ligand bears another functional group capable of undergoing further reactions of synthetic significance. For such a purpose, we have selected the formyl group, a derived amino(imino)-Schiff base and the cyano group as the other functional motifs. Hence, we have applied the diazido complex *cis*-[Pt(N₃)₂(PPh₃)₂] as the source of the metallazide and the following functionalized organonitriles as sources of further functional moieties: 4-cyanobenzaldehyde N≡CC₆H₄(4-CH=O) for the *formyl*/phenyltetrazolato–Pt products and an amino Schiff base derivative, and dicyanobenzenes C₆H₄(C≡N)₂ for the *cyanophenyl*tetrazolato–Pt compounds. These reactions are now reported, together with some side results.

Results and Discussions

Reactions of *cis*-[Pt(N₃)₂(PPh₃)₂] (1) with 4-Cyanobenzaldehyde (2)

Treatment of the diazidoplatinum(II) complex *cis*-[Pt(N₃)₂(PPh₃)₂] (1) with 4-cyanobenzaldehyde (2) in refluxing DMF for 12 h furnishes the *N*²*N*²-bonded bis[5-(4-formylphenyl)tetrazol-2-ato]platinum(II) complex *trans*-[Pt{N₄CC₆H₄(4-CH=O)}₂(PPh₃)₂] (3a) as the major product, isolated as a white crystalline solid in moderate yield (ca. 55%; Scheme 1). The reaction can be greatly accelerated under microwave irradiation (1 h, 100 °C, 300 W), leading to the same product in comparable yield. Formylphenyltetrazolato complex 3a is formed by [2+3] cycloaddition of 4-cyanobenzaldehyde (2) with the ligated azide. A *cis*-to-*trans* isomerization also occurred upon heating, indicating that the *trans* isomer of the bis(formylphenyltetrazole) product is thermodynamically more favourable than the *cis* one. Related thermal isomerizations of *cis*-[PtCl₂(RCN)₂] into *trans*-[PtCl₂(RCN)₂] have been reported previously.^[19] A *trans*-azido to *cis*-tetrazolato conversion is known^[20] for a palladium(II) centre. Apart from *N*²*N*²-bonded bistetrazolato complex 3a, the described reaction leads also to the formation of a smaller amount (ca. 11%) of *N*¹*N*²-bonded isomer 3b (Scheme 1). The two isomeric products 3a and 3b are detected by TLC on silica gel (spots with different *R_f* values), and they were separated by column chromatography on silica gel and isolated as a white solid (for 3a) and an oily product (for 3b, see the Experimental Section).

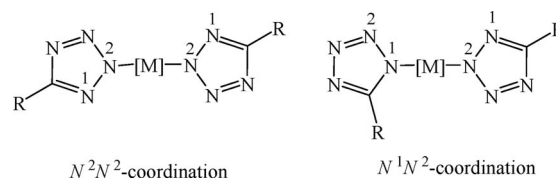
Complexes 3a and 3b were characterized by elemental analyses, IR, ¹H NMR, ¹³C{¹H} NMR and ³¹P{¹H} NMR spectroscopy and X-ray crystal structural analysis (for 3a). Their IR spectra display a band at 1611 cm⁻¹ (for 3a) and 1627 cm⁻¹ (for 3b) due to the tetrazolato ring,^[17,18] quite distinct from the typical azide band at 2055 cm⁻¹ in 1. The triphenylphosphane ligands are detected by their characteristic bands at 1436 and 695 cm⁻¹. No band that could be assigned to N–H stretching or bending was observed, indicating the anionic nature of the tetrazolato ligand. The CO



Scheme 1. *N*²*N*²-Bonded isomer 3a is the major product.

group of the formyl moiety is detected at ca. 1700 cm⁻¹. The ³¹P{¹H} NMR spectra of 3a and 3b exhibit a singlet with platinum satellites at δ = 16.6 (*J*_{Pt,P} = 2686 Hz) and 17.0 (*J*_{Pt,P} = 2650 Hz) ppm, respectively. These coupling values clearly show the *trans* configuration of the phosphanes.^[17,18,21]

Contrary to the alkyl tetrazolato complexes obtained from an alkyl nitrile, which show several ³¹P{¹H} NMR resonances of different isomers,^[17c] the sole singlet resonance of complex 3a indicates the existence of only the *N*²-coordination for each formylphenyltetrazolato ligand (Scheme 2, left), which was also confirmed by X-ray diffraction analysis (see below). This type of *N*-coordination corresponds to the minimal steric congestion of both bulky tetrazolato rings.



Scheme 2.

Two different molecular structures were obtained for the complex *trans*-[Pt{N₄CC₆H₄(4-CH=O)}₂(PPh₃)₂] (3a and 3a'; Table 1, Figure 1), which differ in the fact that the latter includes a disordered reagent molecule in a void (see Experimental Section). Interestingly, such a fact has almost no significant consequences in distances, angles or packing. The Pt environment in these complexes is square-planar with *trans*-positioned *N*² coordinated tetrazolato ligands.

Each tetrazolato cycle lay in a plane that forms a small angle of 6.63 (**3a**) or 8.29° (**3a'**) with the attached formylphenyl group, thus indicating an extended π -electron conjugation consistent with the thermodynamic stability of the compound. Moreover, the plane that contains one of the phosphane phenyls (C21–C26 phenyl in **3a** or C11–C16 phenyl in **3a'**) and that of the tetrazolate ring make an angle of 27.31 (**3a**) or 26.84° (**3a'**) and mutually interact through their π -electronic clouds (centroid–centroid distances of 3.593 Å, in both cases). All bond lengths and angles are within the values described for related compounds.^[17c,17d,18]

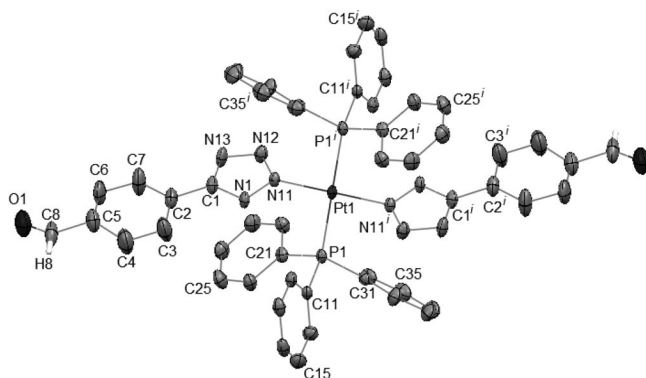
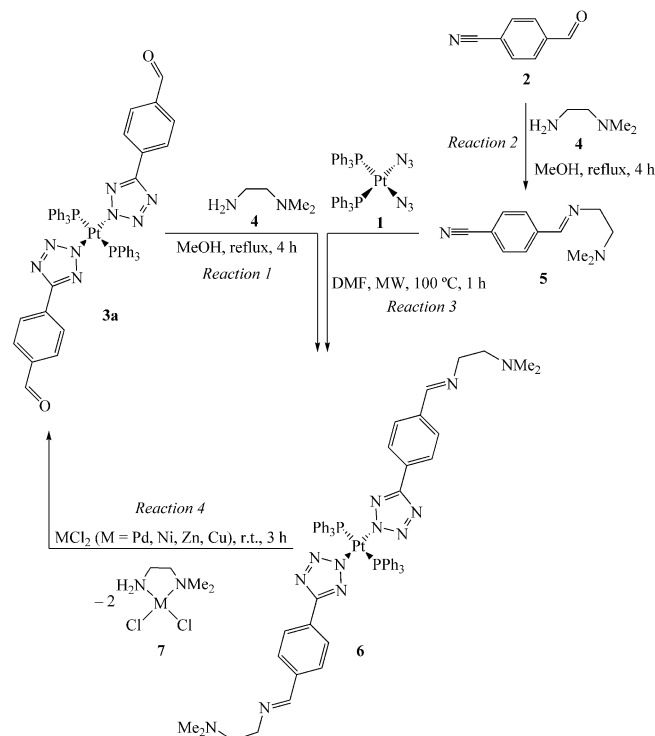


Figure 1. Molecular structure of **3a** with atomic numbering scheme. Thermal ellipsoids are drawn at 30% probability. Symmetry operation to generate equivalent atoms: 1 $-x$, 2 $-y$, $-z$. Selected bond lengths [Å] and angles [°]: Pt1–N11 2.003(3), Pt1–P1 2.3336(11); P1–Pt1–N11 91.47(11), P1–Pt1–N11' 88.53(11).

The ¹H and ¹³C NMR spectra of complex **3b** show chemical shift values ($\Delta\delta \approx 0.08$) that are close to those of N^2N^2 -bonded isomer **3a**, whereas the ³¹P{¹H} NMR singlet of **3b** (at 0.4 ppm lower field than that of **3a**) indicates also the existence of a single but different isomer. We believe this concerns the N^1N^2 -coordination mode (Scheme 2, right) on account of similar results we recently reported in the case of the reaction of the diazidoplatinum(II) complex with 2-cyanopyridine, giving the N^1N^2 isomer of the bis(pyridyltetrazolate) complex.^[18] Unfortunately, all our attempts to obtain crystals of **3b** suitable for X-ray structural analysis failed.

In an attempt to introduce further coordination sites into *trans*-[Pt{N₄CC₆H₄(4-CH=O)}₂(PPh₃)₂] (**3a**), it was treated with 2-dimethylaminoethylamine [H₂NCH₂CH₂NMe₂] (**4**), 2 equiv.] in refluxing methanol for 4 h to give the corresponding Schiff base derivative N^2N^2 -bonded bis[(*E*)-5-(4-{[2-(dimethylamino)ethylimino]methyl}phenyl)tetrazol-2-ato]platinum(II) complex *trans*-[Pt{N₄CC₆H₄(4-CH=NCH₂CH₂NMe₂)}₂(PPh₃)₂] (**6**) in good yield (ca. 78%; Scheme 3, reaction 1). New compound **6** was characterized by elemental analysis and IR, ¹H NMR, ¹³C{¹H} NMR and ³¹P{¹H} NMR spectroscopy. The IR spectrum does not show the typical C=O band and displays a new strong band at 1642 cm⁻¹ of the formed imine C=N group. In the ¹H NMR spectrum, the CH=N is detected at $\delta = 8.29$ ppm; the ¹³C NMR resonances at $\delta = 161.5$ and 163.5 ppm confirm the presence of the imino and tetrazolato moieties, respectively. The ³¹P{¹H} NMR spectrum exhibits a singlet

at $\delta = 16.5$ ppm with Pt satellites that have a characteristic J value ($J_{\text{Pt,P}} = 2710$ Hz) for a *trans* configuration of the phosphanes.^[17,18,21]



Scheme 3.

An alternative route to obtain complex **6** involves the reverse order of reactions as follows. Firstly, starting 4-cyanobenzaldehyde (**2**) reacts with 2-dimethylaminoethylamine (**4**) in refluxing methanol for 4 h to give exclusively the *E* isomer of the condensation product 4-{[2-(dimethylamino)ethylimino]methyl}benzonitrile (**5**) in good yield (ca. 77%; Scheme 3, reaction 2). Secondly, **5** is allowed to react with the diazidoplatinum(II) complex *cis*-[Pt(N₃)₂(PPh₃)₂] (**1**) under focused microwave irradiation (1 h, 100 °C, 300 W) to afford final complex **6** in moderate yield (ca. 52%; Scheme 3, reaction 3).

Iminobenzonitrile compound **5** was characterized by MS (ESI) and IR, ¹H NMR and ¹³C{¹H} NMR spectroscopy and, in the protonated amine form (**5**·HCl), by single-crystal X-ray diffraction. In the IR spectrum, $\nu(\text{N}\equiv\text{C})$ appears at a wave number (2229 cm⁻¹) that is identical to that observed (2230 cm⁻¹) for starting nitrile **2**, whereas the detection of a new band at 1646 cm⁻¹ assigned to $\nu(\text{C}=\text{N})$ confirms the formation of the imine group. In the ¹H NMR spectrum, the CH=N resonance is detected at $\delta = 8.24$ ppm. In the ¹³C{¹H} NMR spectrum, the C=N and N≡C carbon atoms are observed at $\delta = 159.6$ and 118.1 ppm, respectively.

The single-crystal X-ray diffraction analysis of the product of the slow recrystallization of **5** from chloroform (see Supporting Information) indicated the formation of the protonated amine salt N≡CC₆H₄(4-CH=NCH₂-

$\text{CH}_2\text{NHMe}_2^+\text{Cl}^-$ (**5**·HCl, where HCl was conceivably formed upon decomposition of chloroform) and confirmed the *E* configuration. The cyano and the imine bond lengths [1.131(3) and 1.257(3) Å, respectively] together with their NCC and CNC angles [178.2(3) and 118.27(19)°, respectively] are in accord with the known average values.^[22]

It is worthy to indicate that the reaction of 4-cyanobenzaldehyde (**2**) with 2-dimethylaminoethylamine (**4**) in refluxing methanol for an extended period (16 h instead of the 4 h required for the formation of pure *E* isomer **5**), proceeds further to give a mixture of the *E* and *Z* isomers of **5**. The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of the *E/Z* mixture show two sets of signals with close chemical shift values ($\Delta\delta \approx 0.07$ and 0.8, respectively). The reaction of **2** with **4** using dichloromethane instead of methanol under the same experimental conditions led to the formation of **5** in a very poor yield, along with a number of uncharacterized products.

The use of a coordination compound bearing a ligand with a potentially available coordinating site is a known strategy to generate mixed-metal complexes.^[23] We have tested bis(dimethylaminoethyliminotetrazolate) complex **6** containing two *N-N* chelating groups, whereas MCl_2 ($\text{M} = \text{Pd}, \text{Ni}, \text{Zn}, \text{Cu}$) were taken as second metal sources. A dichloromethane solution of complex **6** was treated dropwise with a methanolic solution of MCl_2 , at room temperature for 3 h, to afford a colourless ($\text{M} = \text{Zn}$) or a clear blue ($\text{M} = \text{Cu}$) solution from which, however, only the bis[5-(4-formylphenyl)tetrazol-2-ate] complex **3a** could be isolated, formed by metal-promoted hydrolysis of the two imino groups of **6** (Scheme 3, reaction 4). The same product was obtained in the case of the reaction of **6** with PdCl_2 or NiCl_2 in acetone at room temperature for 3 h. In all cases the formation of **3a** was confirmed by IR, ^1H NMR, $^{13}\text{C}\{^1\text{H}\}$ NMR and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. The use of another anion in the metal source, for example, copper nitrate instead of CuCl_2 , also gives hydrolysis product **3a**. Hydrolysis of Schiff bases is frequently encountered in the

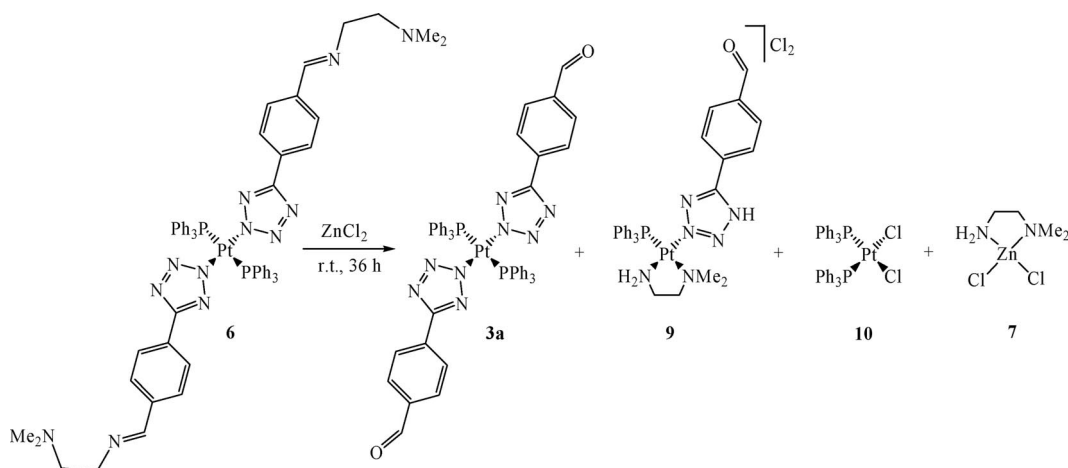
synthesis of their complexes and sometimes is used for the formation of new compounds.^[24] Hence, our observations may be useful in this field.

The metal (M) assisted hydrolysis of **6**, leading to **3a**, also affords $[\text{MCl}_2(\text{NH}_2\text{CH}_2\text{CH}_2\text{NMe}_2)]$ (**7**; Scheme 3, reaction 4), as proved by the identical ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR signals of the crude product of the reaction of **6** with ZnCl_2 with those observed for $[\text{ZnCl}_2(\text{NH}_2\text{CH}_2\text{CH}_2\text{NMe}_2)]$ (**7**) prepared separately by reaction of 2-dimethylaminoethylamine $\text{NH}_2\text{CH}_2\text{CH}_2\text{NMe}_2$ (**4**) with ZnCl_2 in MeOH (see Experimental Section). The structure of **7** was confirmed by X-ray diffraction analysis (see Supporting Information).

The reaction of **6** with ZnCl_2 for an extended period of time (36 h instead of 3 h) proceeds further to give the substitution products $[\text{Pt}\{\text{HN}_4\text{CC}_6\text{H}_4(4\text{-CH=O})\}(\text{NH}_2\text{CH}_2\text{CH}_2\text{NMe}_2)(\text{PPh}_3)]\text{Cl}_2$ (**9**) and *cis*- $[\text{PtCl}_2(\text{PPh}_3)_2]$ (**10**; Scheme 4), probably formed by ligand metathesis (cross-exchange) of the bis(tetrazolato)- Pt^{II} complex **3a** with the dichlorodiamino- Zn^{II} compound **7**. Moreover, in the formation of **9**, protonation of the ligated tetrazolate has also occurred to yield the corresponding neutral tetrazole ligand.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction mixture shows resonances at $\delta = 16.6, 17.0$ and 14.2 ppm, with relative intensities of 1:0.7:0.2, for **3a**, **9** and **10**, correspondingly. The formulation of **10** as the known^[25] *cis*- $[\text{PtCl}_2(\text{PPh}_3)_2]$ was unambiguously established by X-ray structural analysis and by the identical $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum to that of a sample of this compound which was prepared separately by reaction of K_2PtCl_4 with PPh_3 .

Crystallographic analysis of compound **9** indicates that its asymmetric unit consists of one Pt^{II} complex cation, two chloride anions and three molecules of water (Figure 2), with the metal centre in a square planar environment. The tetrazole ligand bears the H atom at the N13 nitrogen. On account of the chelating diamine, its N–Pt–N angle of $83.6(2)^\circ$ is smaller than the ideal value. Moreover, the Pt–N bond lengths involving this ligand [2.036(5) and



Scheme 4.

2.141(5) Å] are longer than that involving the tetrazole [2.005(6) Å], as expected. The other bond lengths and angles are in the common range for such a type of complex.^[22] An intramolecular π interaction was found in the structure of **9** that involves the tetrazolate and the C21–C26 phosphane ring; the distance between these planes is of 3.73 Å (centroid–centroid) with an interplanar angle of 16.93°.

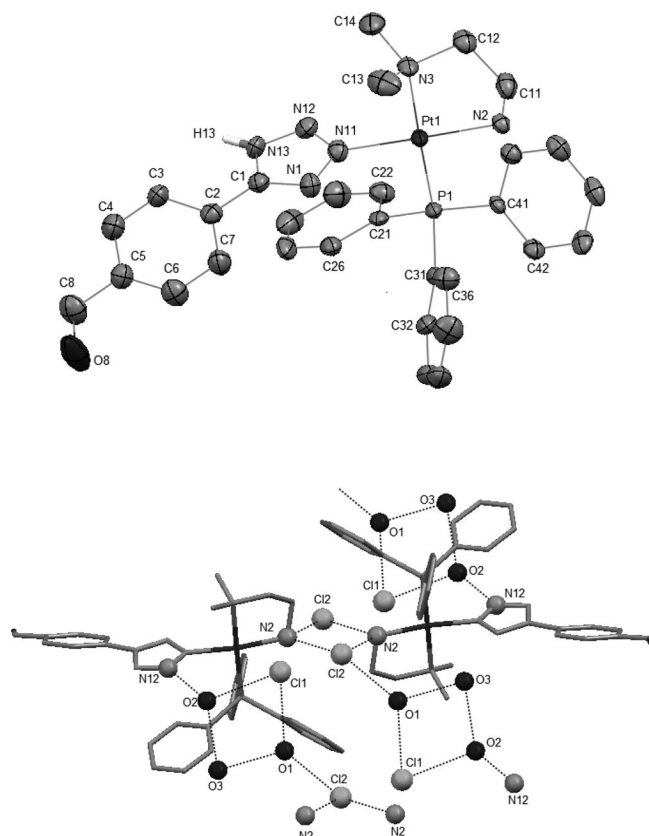


Figure 2. Molecular structure of **9**·3H₂O (top) with atomic numbering scheme (ellipsoids are drawn at 30% probability) and hydrogen-bonding interactions (bottom). Selected bond lengths [Å] and angles [°]: Pt1–P1 2.2558(15), Pt1–N2 2.036(5), Pt1–N3 2.141(5), Pt1–N11 2.005(6), N2–C11 1.486(8), N3–C12 1.509(9), N2–Pt1–N11 173.2(2), P1–Pt1–N3 177.16(17), P1–Pt1–N2 95.44(15), N2–Pt1–N3 83.6(2), N3–Pt1–N11 91.8(2). Intermolecular hydrogen bonds (dotted lines), D–H···A [*d*(D···A), Å; $\angle$ (DHA), °]: O1–H1A···O3 [2.774(10), 140.00], O1–H1B···Cl2 [2.880(9), 154.00], O2–H2A···N12ⁱ [3.029(10), 178.00], O2–H2B···Cl1 [3.180(7), 162.00], N2–H2C···Cl2 [3.142(7), 150.00], N2–H2D···Cl2ⁱⁱ [3.032(7), 142.00], O3–H3A···N1 [3.092(8), 161.00], O3–H3B···O2 [2.836(9), 165.00]. Symmetry codes to generate equivalent atoms: *i*: –1 + *x*, *y*, *z*; *ii*: 2 – *x*, 1 – *y*, –*z*.

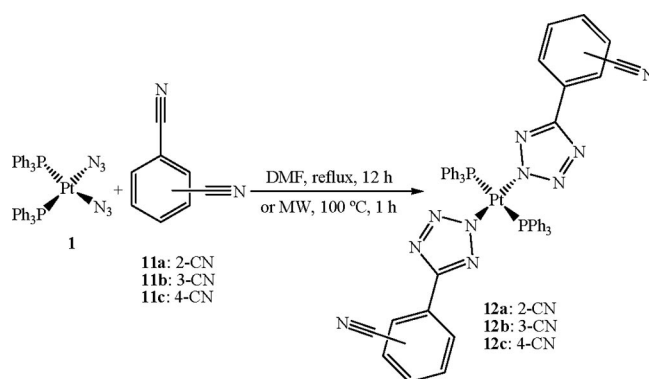
The molecules of **9** are organized into dimers by N–H···Cl hydrogen-bonding interactions (Figure 2); the N2 amine hydrogen atoms from two adjacent molecules of **9** are directed towards two Cl2 chloride anions; the H···Cl distances for these interactions (H2C···Cl2 2.31 and H2D···Cl2 2.25 Å) are well below the van der Waal's radii sum (2.95 Å). These dimers are interconnected by means of a bridging tetranuclear (H₂O)₃Cl water chloride cluster, which is hydrogen bonded to the dangling Cl2 anion, from

one side, and to the tetrazole N12 nitrogen from a vicinal dimer, therefore forming a 2D network. These sheets broaden to a third dimension by means of weak C–H··· π interactions: the hydrogen atoms, H25, at the 3-positions of phosphane phenyls from one sheet are aimed at the π -clouds of the phosphane C31–C36 rings from an adjacent sheet (H···centroid distance of 3.27 Å with a C25–H25···centroid angle of 152.48°); additionally, the H32 at the 2-positions of phosphane phenyls interact with the π -clouds of the formylphenyl rings (C2–C7) (H···centroid distance of 2.90 Å with a C32–H32···centroid angle of 142.85°).

Within the water–chloride cluster in **9** the O···O and O···Cl distances (average 2.805 and 3.067 Å, respectively) are similar to those found in water (2.85 Å) and lie in the range found in other water clusters^[26] or hybrid water chloride assemblies.^[27]

Reactions of *cis*-[Pt(N₃)₂(PPh₃)₂] (**1**) with Dicyanobenzenes **11**

In the second part of this work, we studied the reactions of the diazidoplatinum(II) complex *cis*-[Pt(N₃)₂(PPh₃)₂] (**1**) with an excess amount of unsubstituted dicyanobenzenes **11** [1,2-C₆H₄(CN)₂ **11a**, 1,3-C₆H₄(CN)₂ **11b**, 1,4-C₆H₄(CN)₂ **11c**] in refluxing DMF for 12 h or under microwave irradiation (1 h, 100 °C, 300 W), affording, by [2+3] cycloaddition of the ligated azide with one cyano group in **11**, the corresponding *N*²*N*²-bonded bis[5-(cyanophenyl)tetrazol-2-ate] *trans*-[Pt(N₄CC₆H₄R)₂(PPh₃)₂] complexes **12** (R = 2-CN **12a**, 3-CN **12b**, 4-CN **12c**), isolated as white crystalline solids in moderate to good yields (ca. 50–82%; Scheme 5). However, the reaction of **1** with **11a** in a 1:1 ratio leads to reduction of the platinum centre and no product of cycloaddition was detected.



Scheme 5.

However, the reactions of diazido complex **1** with substituted phthalonitriles R¹R²R³R⁴C₆(CN)₂-1,2 such as 4-nitrophthalonitrile (R² = NO₂, R¹ = R³ = R⁴ = H), tetrachlorophthalonitrile (R¹ = R² = R³ = R⁴ = Cl) or malononitrile CH₂(CN)₂ under focused microwave irradiation (1 h, 100 °C, 300 W) afford a number of uncharacterized products along with species of degradation.

New complexes **12** were characterized by elemental analysis and IR, ^1H NMR, $^{13}\text{C}\{^1\text{H}\}$ NMR and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy and also by X-ray structural analysis for compound **12a**. The IR spectra show the typical $\text{C}\equiv\text{N}$ band at ca. 2230 cm^{-1} and display a new strong band within the $1615\text{--}1670\text{ cm}^{-1}$ range due to the tetrazole ring.^[17] No band assigned to N–H stretching or bending was observed, in contrast with those due to the triphenylphosphane ligands at ca. 1436 and 696 cm^{-1} , which are also shown by the starting complex **1**. In the ^1H NMR spectra, the aromatic protons are detected in the $\delta = 7.14\text{--}7.67\text{ ppm}$ range and the ^{13}C NMR resonances at ca. $\delta = 118$ and 162 ppm confirm the presence of the cyano and the tetrazolato moieties, respectively. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra exhibit a singlet at $\delta = 16.3\text{--}16.9\text{ ppm}$ with platinum satellites, whose $J_{\text{Pt,P}}$ values ($2674\text{--}2683\text{ Hz}$) show the *trans* configuration of the phosphanes,^[17,18,21] and the singlet resonance indicates the existence of only one type of coordination for each (cyanophenyl)tetrazolato ligand. The crystal structure analysis (Figure 3) of **12a** shows that the platinum atom is in an inversion centre and lies in a slightly distorted N_2P_2 square-planar environment with the tetrazolate ligands with the most sterically favourable N^2N^2 -coordination type.^[17,18] These ligands are almost planar; indeed, the interplanar angle between the substituted phenyl ring and the adjacent tetrazolate ring is of 8.80° , whereas the angle between the N_4C_1 rings is as small as 0.43° . Bond lengths and angles around the platinum atom are identical to those of compound **3a** and to other related complexes.^[17]

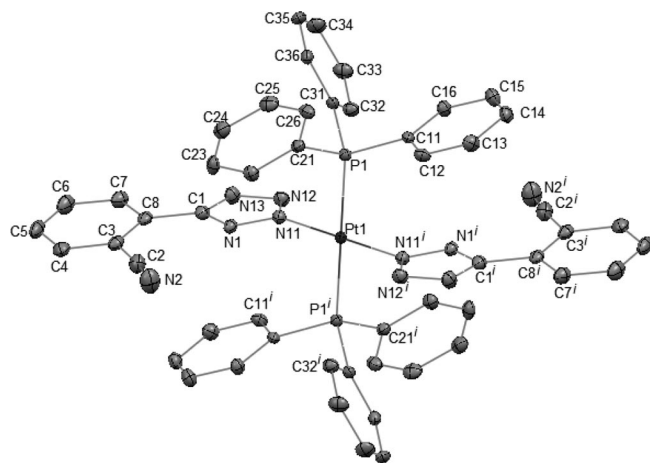


Figure 3. Thermal ellipsoid view of **12a** with atomic numbering scheme. Thermal ellipsoids are drawn at 30% probability. Symmetry transformations used to generate the equivalent atoms *i*: $-x$, $-y$, $-z$. Selected bond lengths [Å] and angles [°]: Pt1–N11 2.018(3), Pt1–P1 2.3403(10), N11–Pt1–N11' 180.0, N11–Pt1–P1' 92.30(9), N11–Pt1–P1 87.70(9), P1–Pt1–P1' 180.0.

The structure of **12a** is also stabilized by intramolecular π – π stacking interactions between the planes of the C11–C16 phenyl and the tetrazolate rings (centroid–centroid distance of 3.625 Å), as well as by an intermolecular edge-to-face C13–H13 $\cdots\pi$ (C31–C36 ring) interaction (H $\cdots$ centroid distance of 3.455 Å) with a C13–H13 $\cdots$ centroid angle of 128.17° .

Conclusions

This study has achieved the easy synthesis of functionalized tetrazolato ligands that are derived upon [2+3] cycloaddition of a ligated azide with a suitable functionalized organonitrile. Hence, the cycloaddition reaction between a Pt^{II} -bound azide and 4-cyanobenzaldehyde provides a convenient route to the formylphenyltetrazolato ligand, which, bearing a formyl moiety, is an expected handy tool towards further introduction of a Schiff base character in the complex. However, the Schiff base undergoes hydrolysis upon further reaction with the metal salts studied. This hydrolysis is fast in comparison with the formation of products of substitution of the tetrazolato ligands. Moreover, the cycloaddition reaction of a Pt^{II} -bound azide and an unsubstituted dicyanobenzene affords the ligated cyanophenyltetrazolato.

Both the azide ligands of the starting diazido Pt^{II} complex underwent [2+3] cycloaddition with the nitriles, and thus, bis(functionalized tetrazolato)– Pt^{II} complexes were always obtained. Although the sterically favourable N^2N^2 -bonded isomer was the exclusive product in the case of the coupling with a dicyanobenzene, the less favourable and uncommon N^1N^2 -bonded isomer was also formed, as a minor product, from the coupling with 4-cyanobenzaldehyde. The extension of the study to the synthesis of other functionalized tetrazolato complexes is currently under consideration in our laboratory.

Experimental Section

Material and Instrumentation: Solvents and reagents were obtained from commercial sources (Aldrich) and used as received. For TLC, Merck Silica gel 60F₂₅₄ plates were used. C, H and N elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. ^1H and ^{13}C spectra (in CDCl_3 , $[\text{D}_4]\text{-MeOD}$ or $[\text{D}_6]\text{DMSO}$) were measured with Bruker Avance II 300 and 400 MHz (UltraShield™ Magnet) spectrometers at ambient temperature. ^1H , ^{13}C and ^{31}P chemical shifts (δ) are expressed in ppm relative to $\text{Si}(\text{Me})_4$ (^1H and ^{13}C) or 85% H_3PO_4 (^{31}P). Infrared spectra ($4000\text{--}400\text{ cm}^{-1}$) were recorded with a Bio-Rad FTS 3000MX instrument in KBr pellets. 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 $10\text{ }\mu\text{L min}^{-1}$. 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.

Reaction of *cis*-[Pt(N₃)₂(PPh₃)₂] (**1**) with 4-Cyanobenzaldehyde (**2**)

Method A: A solution of **1** (200 mg, 0.249 mmol) in DMF (4 mL) was added at room temperature to 4-cyanobenzaldehyde (**2**; 326 mg, 2.49 mmol), and the mixture was heated at reflux for 12 h whereupon the solvent was removed in vacuo. The crude residue was purified by column chromatography on silica ($\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$, 10:1 for N^1N^2 -bonded isomer **3b**; $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$, 5:1 for the N^2N^2 -

bonded isomer **3a**), followed by evaporation of the solvent in vacuo to give the final oily product **3b** or white solid **3a**.

Method B: Under these conditions, 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. After evaporation of the solvent in vacuo to dryness, the crude residue was purified as indicated above.

Crystals of **3a** suitable for X-ray analysis were obtained by slow evaporation of a chloroform solution, whereas crystals of **3a'** were formed upon slow evaporation of a diethyl ether suspension.

trans-[Pt{N₄CC₆H₄(4-CH=O)}₂(PPh₃)₂] (N¹N²-Bonded Isomer **3b):** Yield: 29.18 mg, 11% (method A); 26.53 mg, 10% (method B). IR: $\tilde{\nu}$ = 1699 (C=O), 1627 (C=N) cm⁻¹. ¹H NMR (CDCl₃): δ = 7.25–7.83 (m, 38 H, CH_{aromatic}), 9.99 (s, 2 H, CH=O) ppm. ¹³C{¹H} NMR (CDCl₃): δ = 126.6–135.8 (C_{aromatic}), 163.2 (C=N), 191.9 (C=O) ppm. ³¹P{¹H} NMR (CDCl₃): δ = 17.0 (*J*_{Pt,P} = 2650 Hz) ppm. C₅₂H₄₀N₈O₂P₂Pt (1065.95): calcd. C 58.59, H 3.78, N 10.51; found C 58.17, H 3.98, N 10.27.

trans-[Pt{N₄CC₆H₄(4-CH=O)}₂(PPh₃)₂] (N²N²-Bonded Isomer **3a):** Yield: 145.89 mg, 55% (method A); 148.55 mg, 56% (method B). IR: $\tilde{\nu}$ = 1701 (C=O), 1611 (C=N) cm⁻¹. ¹H NMR (CDCl₃): δ = 7.23–7.82 (m, 38 H, CH_{aromatic}), 9.99 (s, 2 H, CH=O) ppm. ¹³C{¹H} NMR (CDCl₃): δ = 126.5–136.0 (C_{aromatic}), 163.1 (C=N), 191.9 (C=O) ppm. ³¹P{¹H} NMR (CDCl₃): δ = 16.6 (*J*_{Pt,P} = 2686 Hz) ppm. C₅₂H₄₀N₈O₂P₂Pt (1065.95): calcd. C 58.59, H 3.78, N 10.51; found C 58.13, H 3.96, N 10.16.

Reaction of trans-[Pt{N₄CC₆H₄(4-CH=O)}₂(PPh₃)₂] (3a**) with 2-Dimethylaminoethylamine (**4**):** To a solution of **3a** (40.0 mg, 0.037 mmol) in MeOH (10 mL) was added 2-dimethylaminoethylamine (**4**; 7.3 mg, 0.083 mmol). The resulting mixture was heated at reflux for 4 h, and the progress of the reaction was monitored by TLC. The solution is then dried in vacuo, and the crude residue was purified by column chromatography on silica (CH₂Cl₂/Et₂O, 10:1) followed by evaporation of the solvent in vacuo to give final white solid **6**.

trans-[Pt{N₄CC₆H₄(4-CH=NCH₂CH₂NMe₂)₂(PPh₃)₂] (6**):** Yield: 35.31 mg, 78%. IR: $\tilde{\nu}$ = 1613 and 1642 (C=N) cm⁻¹. ¹H NMR (CDCl₃): δ = 2.32 (s, 12 H, CH₃), 2.66 (t, *J*_{H,H} = 6.8 Hz, 4 H, CH₂CH₂), 3.75 (t, *J*_{H,H} = 6.8 Hz, 4 H, CH₂CH₂), 7.18–7.65 (m, 38 H, CH_{aromatic}), 8.29 (s, 2 H, CH=N) ppm. ¹³C{¹H} NMR (CDCl₃): δ = 45.8 (CH₃), 59.8 (CH₂), 60.1 (CH₂), 126.3–135.9 (C_{aromatic}), 161.5 (CH=N), 163.5 (C=N) ppm. ³¹P{¹H} NMR (CDCl₃): δ = 16.5 (*J*_{Pt,P} = 2710 Hz) ppm. C₆₀H₆₀N₁₂P₂Pt (1206.22): calcd. C 59.74, H 5.01, N 13.93; found C 59.55, H 5.09, N 13.59.

Reaction of 4-Cyanobenzaldehyde (2**) with 2-Dimethylaminoethylamine (**4**):** To a solution of 4-cyanobenzaldehyde (**2**; 200 mg, 1.524 mmol) in MeOH (25 mL) was added 2-dimethylaminoethylamine (**4**; 161 mg, 1.828 mmol). The solution was heated at reflux for 4 h, and the progress of the reaction was monitored by TLC. The solution was then dried in vacuo, and the crude residue was purified by column chromatography on silica (CH₂Cl₂) followed by evaporation of the solvent in vacuo to give final oily yellow Schiff base product **5**. Recrystallization from CDCl₃ afforded crystals of **5**·HCl suitable for X-ray analysis.

N≡CC₆H₄(4-CH=NCH₂CH₂NMe₂) (5**):** Yield: 236.37 mg, 77%. IR: $\tilde{\nu}$ = 2229 (C≡N), 1646 (C=N) cm⁻¹. ¹H NMR (CDCl₃): δ = 2.19 (s, 6 H, CH₃), 2.56 (t, *J*_{H,H} = 6.6 Hz, 2 H, CH₂CH₂), 3.67 (t, *J*_{H,H} = 6.6 Hz, 2 H, CH₂CH₂), 7.57 (d, *J*_{H,H} = 7.8 Hz, 2 H, CH_{aromatic}), 7.73 (d, *J*_{H,H} = 7.8 Hz, 2 H, CH_{aromatic}), 8.24 (s, 1 H,

CH=N) ppm. ¹³C{¹H} NMR (CDCl₃): δ = 45.4 (CH₃), 59.3 (CH₂), 59.4 (CH₂), 113.4 (C_q, N≡CPh), 118.1 (C≡N), 128.2 (CH_{aromatic}), 131.9 (CH_{aromatic}), 139.6 (C_q, N≡CPh), 159.6 (C=N) ppm. MS (ESI): *m/z* = 202 [M + H]⁺.

Reaction of cis-[Pt(N₃)₂(PPh₃)₂] (1**) with 4-{[2-(Dimethylamino)-ethylimino]methyl}benzonitrile (**5**):** A solution of **1** (20 mg, 0.025 mmol) in DMF (4 mL) was added at room temperature to **5** (50 mg, 0.249 mmol), and the mixture 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 100 °C. After evaporation of the solvent in vacuo to dryness, the crude residue was purified as indicated in method A to give white complex **6** in moderate yield (ca. 16 mg, 52%).

Reaction of trans-[Pt{N₄CC₆H₄(4-CH=NCH₂CH₂NMe₂)₂(PPh₃)₂] (6**) with MCl₂ (M = Pd, Ni, Zn, Cu):** A solution of complex **6** (20 mg, 0.016 mmol) in CH₂Cl₂ (4 mL) was treated dropwise with a solution of ZnCl₂ or CuCl₂ (0.033 mmol) in methanol (4 mL), whilst stirring at room temperature, to afford a colourless (in the case of ZnCl₂) or a clear blue (in the case of CuCl₂) solution. In the case of PdCl₂ or NiCl₂ (0.033 mmol), acetone was used as solvent, giving a yellow (in the case of PdCl₂) or pink (in the case of NiCl₂) solution. The complete hydrolysis of complex **6** to give **3a** and [MCl₂(NH₂CH₂CH₂NMe₂)] (**7**) was observed after 3 h. The reaction of **6** with ZnCl₂ for an extended period of time (36 h instead of 3 h) proceeded further to give [Pt{HN₄CC₆H₄(4-CH=O)}(NH₂CH₂CH₂NMe₂)(PPh₃)Cl₂] (**9**) and cis-[PtCl₂(PPh₃)₂] (**10**). Crystals of **9** and **10** suitable for X-ray analyses were obtained by slow evaporation of the reaction mixture.

Reaction of 2-Dimethylaminoethylamine (4**) with ZnCl₂:** ZnCl₂ (155 mg, 1.134 mmol) was added to a solution of **4** (100 mg, 1.134 mmol) in MeOH (20 mL). The resulting mixture was stirred at room temperature for 3 h. The colourless solution was then dried in vacuo, washed with diethyl ether (3 × 10 mL) and dried in air to give **7** as a white solid. Crystals of **7** suitable for X-ray analysis were obtained by slow evaporation of the reaction mixture.

[ZnCl₂(NH₂CH₂CH₂NMe₂)] (7**):** Yield: 224.62 mg, 88%. IR: $\tilde{\nu}$ = 3329 and 3276 (NH), 2977 (CH) cm⁻¹. ¹H NMR ([D₄]MeOD): δ = 2.55 (s, 6 H, CH₃), 2.68 (t, *J*_{H,H} = 5.4 Hz, 2 H, CH₂CH₂), 2.96 (t, *J*_{H,H} = 5.4 Hz, 2 H, CH₂CH₂) ppm. ¹³C{¹H} NMR ([D₄]MeOD): δ = 38.9 (CH₂), 47.7 (CH₃), 61.4 (CH₂) ppm. MS (ESI): *m/z* = 187 [M – Cl]⁺.

Reactions of cis-[Pt(N₃)₂(PPh₃)₂] (1**) with Dicyanobenzenes (**11**):** A solution of **1** (50 mg, 0.062 mmol) in DMF (4 mL) was added at room temperature to 1,2-dicyanobenzene (**11a**), 1,3-dicyanobenzene (**11b**) or 1,4-dicyanobenzene (**11c**; 80 mg, 0.622 mmol), and the mixture 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 100 °C. After evaporation of the solvent in vacuo to dryness, the crude residue was purified by column chromatography on silica (CH₂Cl₂/Et₂O, 1:1) followed by evaporation of the solvent in vacuo to give final white products **12a**, **12b** or **12c**, respectively. Crystals of **12a** suitable for X-ray analysis were obtained by slow evaporation of a chloroform solution.

trans-[Pt{N₄CC₆H₄(2-C≡N)}₂(PPh₃)₂] (12a**):** Yield: 32.97 mg, 50%. IR: $\tilde{\nu}$ = 2226 (C≡N), 1636 (C=N) cm⁻¹. ¹H NMR (CDCl₃): δ = 7.14–7.60 (m, 38 H, CH_{aromatic}) ppm. ¹³C{¹H} NMR (CDCl₃): δ = 109.7 (C_q, N≡CPh), 118.2 (C≡N), 126.8–135.3 (C_{aromatic}), 161.6 (C=N) ppm. ³¹P{¹H} NMR (CDCl₃): δ = 16.3 (*J*_{Pt,P} = 2674 Hz) ppm. C₅₂H₃₈N₁₀P₂Pt (1059.95): calcd. C 58.92, H 3.61, N 13.21; found C 58.66, H 3.49, N 13.16.

trans-[Pt{N₄CC₆H₄(3-C≡N)}₂(PPh₃)₂] (12b**):** Yield: 41.54 mg, 63%. IR: $\tilde{\nu}$ = 2233 (C≡N), 1670 (C=N) cm⁻¹. ¹H NMR (CDCl₃):

Table 1. Crystal data and structure refinement details for complexes **3a**, **3a'**, **5-HCl**, **7**, **9·3H₂O** and **12a**.

	3a	3a'	5-HCl	7	9·3H₂O	12a
Empirical formula	C ₅₂ H ₄₀ N ₈ O ₂ P ₂ Pt	C ₅₂ H ₄₀ N ₈ O ₂ P ₂ Pt	C ₁₂ H ₁₆ N ₃ ·Cl	C ₄ H ₁₂ Cl ₂ N ₂ Zn	C ₃₀ H ₃₃ N ₆ OPPt·3(H ₂ O)·2Cl	C ₅₂ H ₃₈ N ₁₀ P ₂ Pt
Formula weight	1065.95	1065.95	237.73	224.43	844.62	1059.95
Temperature [K]	150(2)	296(2)	150(2)	292(2)	150(2)	150(2)
Crystal system	triclinic	triclinic	triclinic	monoclinic	triclinic	orthorhombic
Space group	<i>P</i> $\bar{1}$ (No. 2)	<i>P</i> $\bar{1}$ (No. 2)	<i>P</i> $\bar{1}$ (No. 2)	<i>P</i> 2 ₁ / <i>n</i> (No. 14)	<i>P</i> $\bar{1}$ (No. 2)	<i>Pbca</i> (No. 61)
<i>a</i> [Å]	9.9373(3)	9.5137(13)	6.956(3)	10.7714(3)	9.8281(5)	15.8541(16)
<i>b</i> [Å]	10.3579(4)	10.7238(14)	9.365(4)	12.1596(3)	10.0043(5)	14.3050(14)
<i>c</i> [Å]	12.0254(4)	14.129(2)	9.952(4)	14.3987(4)	17.3931(9)	19.2963(19)
α [°]	64.734(2)	70.299(8)	95.27(2)	90	90.8220(10)	90
β [°]	86.929(2)	81.526(7)	97.09(2)	105.1390(10)	90.317(2)	90
γ [°]	78.0670(10)	78.190(7)	96.41(3)	90	105.8040(10)	90
<i>V</i> [Å ³]	1094.33(7)	1323.6(3)	635.6(4)	1820.43(8)	1645.25(14)	4376.3(8)
<i>Z</i>	1	1	2	8	2	4
$\rho_{\text{calcd.}}$ [g cm ⁻³]	1.617	1.337	1.242	1.638	1.705	1.609
μ (Mo- <i>K</i> α) [mm ⁻¹]	3.332	2.755	0.278	3.212	4.520	3.330
Rfls. collected	9658	12711	5318	49806	11446	28585
Rfls. unique	3996	4818	2309	8346	6003	5430
<i>R</i> _{int}	0.0317	0.0342	0.0318	0.0385	0.0229	0.0439
Final <i>R</i> ₁ , <i>wR</i> ₂ (<i>I</i> ≥ 2σ) ^[a]	0.0306, 0.0717	0.0243, 0.0548	0.0370, 0.0896	0.0401, 0.1015	0.0384, 0.0925	0.0277, 0.0614
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0315, 0.0725	0.0242, 0.0548	0.0507, 0.1014	0.0840, 0.1203	0.0481, 0.0983	0.0602, 0.0776
GOF on <i>F</i> ²	1.049	1.035	1.036	1.014	1.077	0.843

[a] $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$.

$\delta = 7.24\text{--}7.81$ (m, 38 H, *CH*_{aromatic}) ppm. ¹³C{¹H} NMR (CDCl₃): $\delta = 112.3$ (C_q, N≡CPh), 118.6 (C≡N), 126.9–134.1 (C_{aromatic}), 162.3 (C=N) ppm. ³¹P{¹H} NMR (CDCl₃): $\delta = 16.9$ (*J*_{Pt,P} = 2683 Hz) ppm. C₅₂H₃₈N₁₀P₂Pt (1059.95): calcd. C 58.92, H 3.61, N 13.21; found C 58.42, H 3.59, N 13.44.

trans-[Pt{N₄CC₆H₄(4-C≡N)}₂(PPh₃)₂] (12c): Yield: 54.07 mg, 82%. IR: $\tilde{\nu} = 2229$ (C≡N), 1615 (C=N) cm⁻¹. ¹H NMR (CDCl₃): $\delta = 7.22\text{--}7.67$ (m, 38 H, *CH*_{aromatic}) ppm. ¹³C{¹H} NMR (CDCl₃): $\delta = 111.7$ (C_q, N≡CPh), 118.8 (C≡N), 126.4–134.5 (C_{aromatic}), 162.6 (C=N) ppm. ³¹P{¹H} NMR (CDCl₃): $\delta = 16.6$ (*J*_{Pt,P} = 2675 Hz). C₅₂H₃₈N₁₀P₂Pt (1059.95): calcd. C 58.92, H 3.61, N 13.21; found C 58.73, H 3.77, N 13.24.

Supporting Information (see footnote on the first page of this article): Molecular structures of compounds **7** and **5-HCl** with bond angles and distances; H-bond geometry in **5-HCl**.

Crystal Structure Determinations: Single crystals of **3a**, **3a'**, **5-HCl**, **7**, **9·3H₂O** and **12a** were obtained as indicated above. Intensity data were collected by using a Bruker AXS-KAPPA APEX II diffractometer with graphite monochromated Mo-*K* α (λ 0.71073) radiation. Data were collected by using omega scans of 0.5° per frame and full sphere of data were obtained. Cell parameters were retrieved by using Bruker SMART software and refined by using Bruker SAINT^[28] on all the observed reflections. Absorption corrections were applied by using SADABS.^[28] Structures were solved by direct methods by using the SHELXS-97 package^[29] and refined with SHELXL-97.^[30] Calculations were performed by using the WinGX System-Version 1.80.03.^[31] All hydrogen atoms were inserted in calculated positions. Least-square refinements with anisotropic thermal motion parameters for all non-hydrogen atoms and isotropic for the remaining atoms were employed. For **3a'**, PLATON/SQUEEZE^[32] was used to correct the data. Potential volume of 239.5 Å³ was found and 68.5 electrons per unit cell worth of scattering were located in a void. The electron count suggests the presence of ca. one cyanobenzaldehyde molecule per unit cell. Table 1 contains the crystallographic parameters for the described crystals. CCDC-733510 (for **3a**), -733511 (for **3a'**), -733512 (for **5-HCl**), -733513 (for **7**), -733514 (for **9·3H₂O**) and -733515 (for **12a**) contain the supplementary crystallographic data for this paper.

These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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