Disponible en ligne sur www.sciencedirect.com
ScienceDirect
C. R. Chimie 12 (2009) 1267–1274
Comptes Rendus Chimie

Full paper/Mémoire

The $[Pd(bipy)]^{2+}$ ''merry-go-round'': Insights into the lability of the Pd–N bond

Partha Pratim Mukhopadhyay [a], Jean-Claude Chambron [a,*], Roland Graff [b]

[a] *ICMUB (UMR n° 5260 of the CNRS), université de Bourgogne, 9, avenue Alain-Savary, BP 47870, 21078 Dijon, France*

[b] *Institut de chimie (UMR n° 7177 of the CNRS), université de Strasbourg, 1, rue Blaise-Pascal, BP 296R8, 67008 Strasbourg, France*

Received 9 February 2009; accepted after revision 9 March 2009
Available online 27 October 2009

Abstract

Two tripods (**1** and **2**) featuring pyrimidinyl pendant arms have been synthesized from 5-(1*H*-pyrazol-3-yl)-pyrimidine (**5**) and 1,3,5-tribromomethylbenzene derivatives. Reaction with three equivalents of $[Pd(bipy)](NO_3)_2$ to form a macrotricycle closed by palladium coordination unexpectedly afforded the mononuclear species $[Pd(\mathbf{1})(bipy)]^{2+}$ and $[Pd(\mathbf{2})(bipy)]^{2+}$. These complexes show fluxional behavior on the ^1H NMR timescale, the $[Pd(bipy)]^{2+}$ fragment hopping between the pyrimidinyl coordinating moieties. The $\Delta G_c^{\ddagger}$'s estimated by the coalescence method are temperature independent, which means that $\Delta S_c^{\ddagger} = 0$. This indicates that the ''merry-go-round'' process of $[Pd(bipy)]^{2+}$ occurs intramolecularly, presumably by nucleophilic attack of the free pyrimidinyl arm to the bound Pd^{2+} center. This phenomenon permits to quantify the lability of the Pd–N coordination bond, the average $\Delta G_c^{\ddagger} \approx \Delta H_c^{\ddagger}$ value being 70 kJ mol^{-1}. ***To cite this article: P.P. Mukhopadhyay et al., C. R. Chimie 12 (2009).***

Keywords: N ligands; Tripodal ligands; Chelates; Palladium; Fluxionality

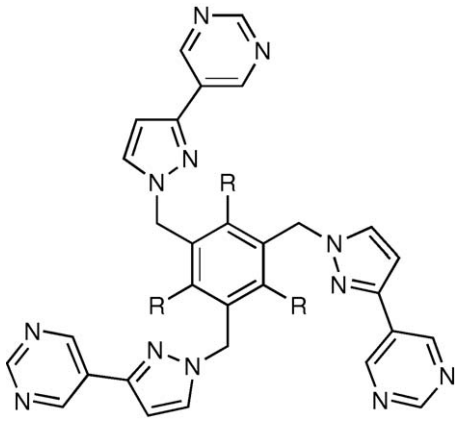
1. Introduction

A great variety of molecular cages have been assembled by complexation of polypyridinyl ligands with the metal cation fragments $[Pd(bipy)]^{2+}$ and $[Pd(en)]^{2+}$ under thermodynamic control, thanks to the lability of non chelating Pd–N bonds in polar solvents [1]. The resulting species can encapsulate guests, which may also play the role of templates [1b,c], and provide a confined environment able to control the regio- and stereoselectivity of various reactions [1d,e] or stabilize otherwise elusive species [1f]. In general, the self-assembled molecular cages form geometrical structures whose sides and vertices (or edges) are occupied by the polypyridinyl ligands and the metal-complex fragments, respectively. Very few examples however, feature systems in which the latter are used to fix the shape of elaborated polytopic ligands [2].

The pyrimidinyl coordinating subunit has been used for the construction of several supramolecular cage structures [3], in particular those incorporating the hypothetical metallacalix[3]arene fragment that would result from cyclotrimerisation of the pyrimidine-Pd^{2+} coordination motif [3a,b,f]. We have synthesized two tris(pyrazol-1-ylmethyl)benzene tripods (**1** and **2**), whose pyrazolyl position 3 is substituted by a 5-pyrimidinyl fragment (Scheme 1). It was expected that bridging of the

* Corresponding author.
E-mail address: Jean-Claude.Chambron@u-bourgogne.fr (J.-C. Chambron).

1631-0748/$ – see front matter
doi:10.1016/j.crci.2009.03.002

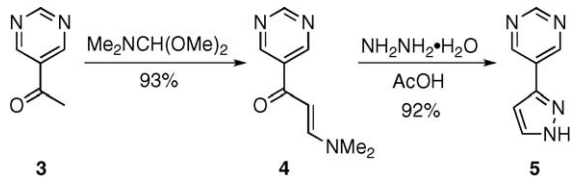


Scheme 1. Structural formulae of tripod ligands **1** and **2**.

pyrimidinyl nitrogen atoms with $[Pd(bipy)]^{2+}$ would form macrotricycles that are metallo-organic analogues of the reported tris (pyrazole)-incorporating organic macrotricycles, which are able to encapsulate NH_4^+, mainly by hydrogen bonding interactions (Scheme S1) [4]. This work shows that, instead of the anticipated $[Pd_3(bipy)_3(\mathbf{1})]^{2+}$ and $[Pd_3(bipy)_3(\mathbf{2})]^{6+}$ macrotricycles, the simple metallamacrocyclic structures $[Pd(\mathbf{1})(bipy)]^{2+}$ and $[Pd(\mathbf{2})(bipy)]^{2+}$ are obtained, indicating that the incorporation of additional $[Pd(bipy)]^{2+}$ complex fragments is unfavorable. The metallamacrocycles display remarkable dynamic properties at the ^1H NMR time-scale: whereas at room temperature they have the expected C_{2v} symmetry, at high temperature (423 K) they show an average C_{3v} symmetry, because the $[Pd(bipy)]^{2+}$ fragment hops between the pyrimidinyl coordinating units. As $\Delta G_c^{\ddagger} \approx \Delta H_c^{\ddagger}$ for this process, the activation enthalpy for the dissociation of the Pd–N bond could be estimated to ≈ 70 kJ mol^{-1}.

2. Results and Discussion

The direct precursor of **1** and **2**, namely 5-(1*H*-pyrazol-3-yl)-pyrimidine (**5**) was synthesized using a classical preparation of pyrazoles, that is condensation of the appropriate β-N,N-dimethylaminoenone with hydrazine (Scheme 2) [5]. Thus 3-(dimethylamino)-1-(5-pyrimidinyl)-2-propen-1-one (**4**), readily obtained (93% yield) by heating 1-(5-pyrimidinyl)-2-ethanone (**3**) [6] in dimethylformamide dimethylacetal, was reacted with hydrazine hydrate in the presence of acetic acid, affording 5-(1*H*-pyrazol-3-yl)-pyrimidine **5** in 92% yield after purification. Noticeably, a very



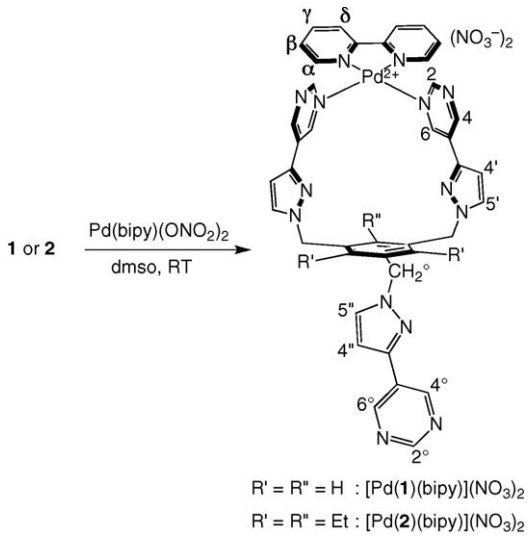
Scheme 2. Preparation of **5** starting from **3**.

efficient preparation of this compound (four steps, 64% overall yield from 5-bromopyrimidine) has been recently reported. It involves the Suzuki cross-coupling reaction between 5-bromopyrimidine and 1-(tetrahydro-2*H*-pyran-2-yl)-1*H*-pyrazole in 92% yield, followed by quantitative hydrolytic cleavage of the THP protection [7].

For the preparation of the target tripod compounds **1** and **2**, pyrazole **5** was deprotonated first [8], and the resulting pyrazolate reacted with the appropriate tris-electrophile, respectively 1,3,5-tribromomethylbenzene [9] and 1,3,5-tribromomethyl-2,4,6-triethylbenzene [10]. The corresponding tripods were obtained in 53% (**1**) and 79% (**2**) yields after chromatographic purification. Both have ^1H NMR spectra in agreement with their expected D_{3h} symmetrical structure.

In the initial complexation experiments, three equivalents of $[Pd(bipy)(ONO_2)_2]$ [11] were added to a solution of tripod **1** in d^6-dmso at room temperature[1]. The ^1H NMR spectrum of the mixture showed the signals of starting $[Pd(bipy)(ONO_2)_2]$ along with those of a species that has not the expected C_3-symmetry, because two sets of signals in 2:1 ratio can be identified for the tripod protons. The same product is formed quantitatively upon using only one equivalent of $[Pd(bipy)(ONO_2)_2]$. Complete analysis of the corresponding ^1H and ^{13}C NMR spectra using $^1H/^1H$ COSY and ROESY, $^1H/^{13}C$ HSQC and HMBC, indicates that the $[Pd(bipy)]^{2+}$ fragment is complexed by two pyrimidinyl subunits of the tripod, thus closing a 20-membered chelate ring, and leaving the third pyrimidinyl arm pendant (Scheme 3). This is corroborated by the comparison of the ^1H NMR spectra of **1** and $[Pd(\mathbf{1})(bipy)]^{2+}$ (Table S1), which shows that the protons of the free pyrimidinyl arm have chemical shifts that are close to those of **1**, whereas protons 2 and 6 *ortho* to the coordinated pyrimidinyl nitrogen are

[1] DMSO turned out to be the only solvent in which homogeneous solutions could be obtained after mixing the reactants. Neither water, nor MeOH and acetone did lead to comparable results. However, $[Pd(\mathbf{1})(bipy)](NO_3)_2$ is soluble in acetone/water mixtures, whereas $[Pd(\mathbf{2})(bipy)](NO_3)_2$ is not.



Scheme 3. Formation of [Pd(**1**)(bipy)]$(NO_3)_2$ and [Pd(**2**)(bipy)]$(NO_3)_2$.

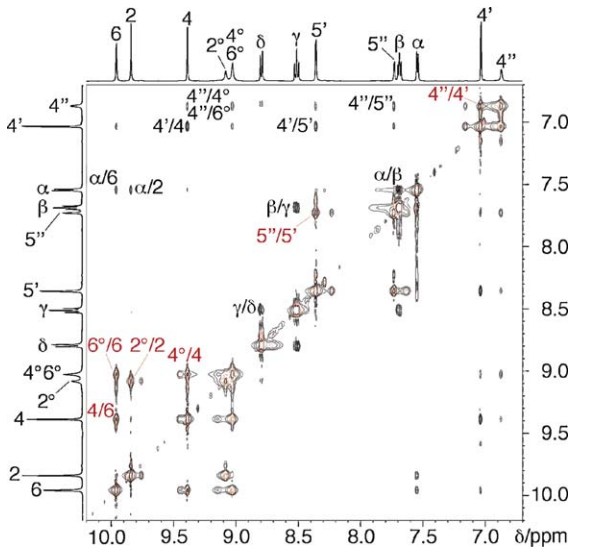


Fig. 1. 2D $^1H/^1H$ NMR EXSY spectrum (aromatic region) of [Pd(**2**)(bipy)]$^{2+}$ in d^6-dmso at 298 K (mixing time: 300 ms). Main NOE correlations and exchange spots are indicated in black and red, respectively.

deshielded by metal coordination ($\Delta\delta = +1.00$ ppm in the latter case). Significantly, intercomponent Nuclear Overhauser effect (NOE) correlations are found between these latter protons and the α protons of the bipy ancillary ligand. 2D $^1H/^1H$ EXSY of [Pd(**2**)(bipy)]$^{2+}$ clearly shows that intramolecular exchange processes are taking place on the NMR timescale (Fig. 1). They exchange homologous protons of the coordinated and uncoordinated pyrimidinyl pendant arms (e.g. 4/4° or 4′/4″), on the one hand, and homologous protons of the bound pyrimidinyl fragments (e.g., 4/6), on the other hand. Accordingly, VT ^1H NMR spectra were recorded in the 293–423 K temperature range. This is illustrated for the case of [Pd(**1**)(bipy)]$^{2+}$ in Fig. 2. As the temperature is increased, all the signals (major and minor) of the tripod protons broaden, giving rise to a sequence of coalescence phenomena (characterized by $\Delta\nu$ in the slow exchange limit, and T_c, Table 1), and sharpen again to form a unique set at 423 K. These results can be interpreted as represented in Scheme 4. Whereas at room temperature the coordination of the [Pd(bipy)]$^{2+}$ complex fragment to the tripod is fixed on the ^1H NMR timescale, this is not the case at high temperature (423 K), where it hops from a pyrimidinyl site to the other. The fluxional process combines ligand and site exchange (resulting from rotation about the 5-C–3′-C bond), and involves Pd–N (pyrimidine) bond cleavage. The computed exchange rates k_c and free activation energies at the coalescence ($\Delta G_c^{\ddagger}$) are collected in Table 1. Remarkably, $\Delta G_c^{\ddagger} = 68.1$ kJ mol^{-1} does not depend on temperature, which indicates that $\Delta S_c^{\ddagger} = 0$. This result proves that the "merry-go-round"

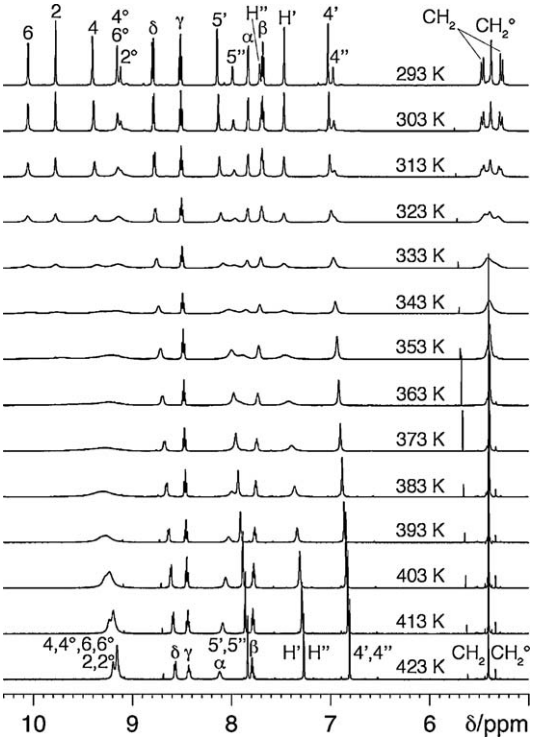


Fig. 2. Sequence of variable temperature spectra of [Pd(**1**)(bipy)]$(NO_3)_2$ in d^6-dmso.

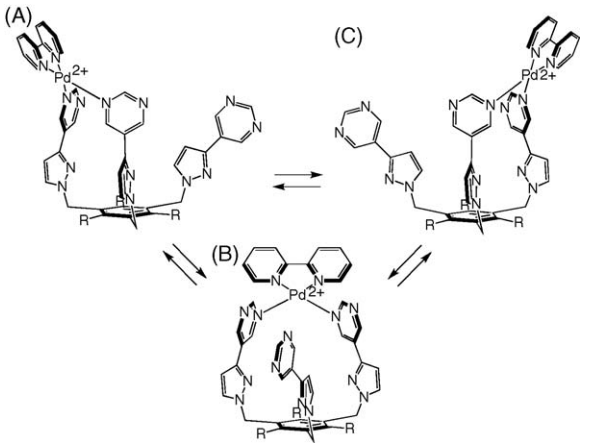
process of [Pd(bipy)]$^{2+}$ takes place intramolecularly, presumably by nucleophilic attack of the free pyrimidinyl arm on the bound Pd^{2+} cation, without complete decoordination of the former.

Table 1
Data obtained from the VT ^{1}H NMR spectra of [Pd(**1**)(bipy)]$^{2+}$ and [Pd(**2**)(bipy)]$^{2+}$.

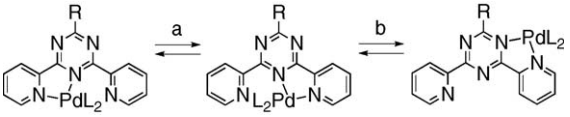
Compound	Probe protons	T_c/K	$\Delta\nu$/Hz[a]	k_c/s^{-1}[b]	$\Delta G_c^{\ddagger}$ /kJ mol^{-1}[c,d]
[Pd(**1**)(bipy)]$^{2+}$	4′, 4″	323	30	67	68
	5′, 5″	338	90	200	68
	H′, H″	343	150	333	68
	4, 4°	343	150	333	68
	2, 2°	358	395	877	68
	6, 6°	363	540	1200	68
[Pd(**2**)(bipy)]$^{2+}$	4′, 4″	358	100	222	72
	CH_2, CH_2°	358	120	267	72
	CH_3′, CH_3″	373	330	733	72
	CH_2′, CH_2″	383	715	1588	71

[a] Frequency difference at the slow exchange limit (293 K).
[b] k_c (s^{-1}) = $(2^{-1/2})\pi\Delta\nu$.
[c] $\Delta G_c^{\ddagger}$ (kJ mol^{-1}) = 2.303 × 8.314 × T_c(10.319 + logT_c–logk_c).
[d] Estimated error: 1 kJ mol^{-1}, assuming $\sigma(T_c)$ = 5 K and $\sigma(\Delta\nu)$ = 5 Hz.

The complex [Pd(**2**)(bipy)]$^{2+}$ exhibits similar behavior, with a slightly higher $\Delta G_c^{\ddagger}$ value (71.5 kJ mol^{-1}). This could arise from the increased rigidity of tripod **2** by comparison with **1**, due to the ethyl substituents, which reduces the mobility of the uncomplexed arm. Fluxional processes involving Pd–N bond rupture have been previously observed in Pd complexes with terpyridines [12a], and 2-pyridyl [12b,c] or *N*-pyrazole [12d]-substituted triazines. For example, in the case of [Pd(*p*-$CF_3C_6F_4$)$_2$(tpt)], where tpt is 2,4,6-tris(2-pyridyl)-1,3,5-triazine, $\Delta G^{\ddagger}$ = 72 kJ mol^{-1} for the 1,4 metallotropic shift (Scheme 5). The average $\Delta G^{\ddagger}$ ≈ 70 kJ mol^{-1} value found for [Pd(**1**)(bipy)]$^{2+}$ and [Pd(**2**)(bipy)]$^{2+}$ is in keeping with that measured in the case of the tpt complex. In addition, our observation that



Scheme 4. The ''merry-go-round'' process of the [Pd(bipy)]$^{2+}$ metal-complex fragment.



Scheme 5. Fluxional processes occurring in [Pd(*p*-$CF_3C_6F_4$)$_2$(tpt)] (L = *p*-$CF_3C_6F_4$, R = 2-pyridyl). (a) 1,4-Metallotropic shift. (b) Rotational hurdling process [12b,c].

$\Delta G^{\ddagger} = \Delta H^{\ddagger}$ allows us to evaluate the enthalpy of activation for the dissociation of the Pd–N (pyrimidine) bond as ≈ 70 kJ mol^{-1}.

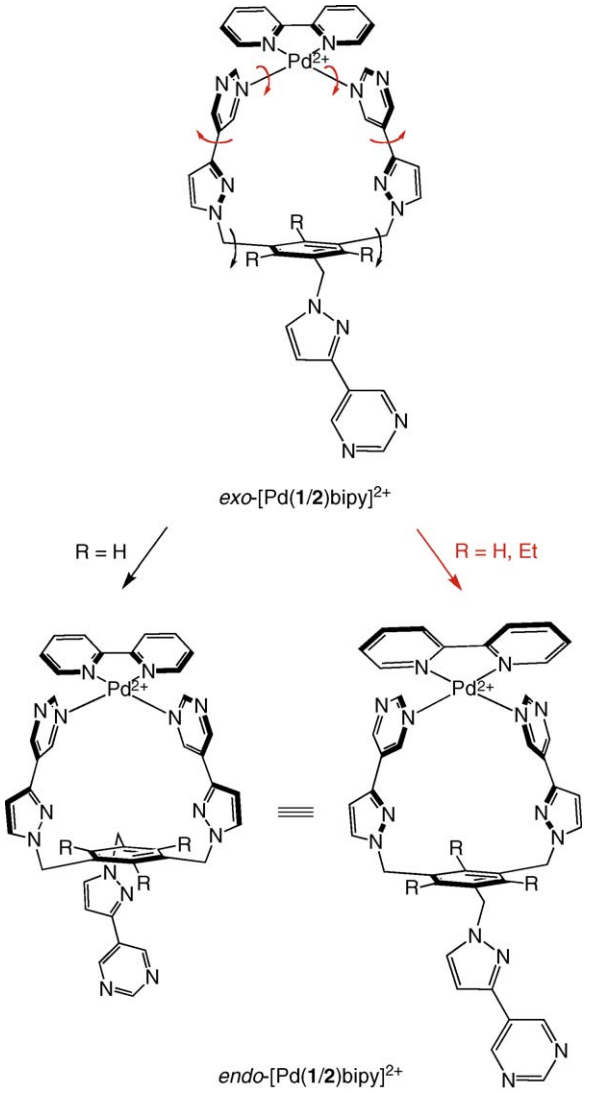
Consideration of molecular models shows that the complexes [Pd(**1**)(bipy)]$^{2+}$ and [Pd(**2**)(bipy)]$^{2+}$ should exist under two different conformations, one in which the [Pd(bipy)]$^{2+}$ metal-complex fragment hangs over the benzene platform and is located on the same side as the free pyrimidinyl arm (*endo* conformation), and the other in which the same fragment and the free pyrimidinyl arm lie on opposite sides (*exo* conformation), as illustrated in Scheme 6. Interconversion between these forms involves concerted rotation about the C (pyrazolyl)–C (pyrimidinyl) and Pd–N (pyrimidinyl) bonds or, in the case of [Pd(**1**)(bipy)]$^{2+}$ only, rotation of the benzene ring about two C (benzene)–C (H_2) bonds, which allows the free pyrimidinyl arm to pass through the metallo-organic macrocycle (Scheme 6). This latter process cannot obviously operate in the case of [Pd(**2**)(bipy)]$^{2+}$ for steric reasons. Unfortunately, as only one species is observed at the lowest temperature possible in d^6-dmso (293 K), these interconversion processes cannot be slowed down in this solvent, preventing one to experimentally demonstrate the possible coexistence of the *endo* and *exo* conformations.

The [Pd(**1/2**)(bipy)]$^{2+}$ complexes have been arbitrarily drawn in the *exo* conformation in Schemes 3 and 4. Nucleophilic attack of the pendant pyrimidinyl arm on *exo*-[Pd(**1/2**)(bipy)]$^{2+}$ will produce necessarily *endo*-[Pd(**1/2**)(bipy)]$^{2+}$. Therefore, exchange between any two of the three structures A, B, and C involves also the *exo*/*endo* interconversion process discussed above.

Finally, the inability of tripods **1** and **2** to take up three [Pd(bipy)]$^{2+}$ complex subunits in dmso deserves being discussed. It could be due to either:

- poor ligand preorganisation;
- steric crowding of the peripheral bipy's;
- lack of stabilization by dmso of the high charge density of the trinuclear species.

Whereas the first hypothesis cannot be ruled out, this is not the case of the second one, as replacing ancillary



Scheme 6. Mechanisms of interconversion between *exo*-[Pd(**1**/**2**)(bipy)]$^{2+}$ and *endo*-[Pd(**1**/**2**)(bipy)]$^{2+}$.

bipyridine by the smaller ethylenediamine leads to the same results. Solvent effects are more likely, as exemplified by the behavior of a C_4-symmetric cavitand bearing four pendant pyrimidinyl arms, which, upon pair wise connection with the same number of [Pd(en)]$^{2+}$ complex fragments forms a metallo-organic macropolycycle [2b]. It must be noted that the desired, C_4-symmetric tetranuclear complex was obtained in the less polar solvent mixture (methanol/water 5:1), whereas the reaction in water led to the incorporation of only two [Pd(en)]$^{2+}$ moieties, producing a C_2-symmetric system. By contrast, C_3-symmetric metallo-organic cage molecules incorporating the metallacalix[3]arene [Pd(pyrimidinyl)]$_3^{6+}$ motif were usually assembled in water [3a-c, 3g]. Whereas this latter solvent was not effective in promoting the formation of the trinuclear complexes because of solubility problems even after prolonged reaction times, future work will explore the effect of increasing the solvent polarity (dmso/water mixtures) or the ionic strength (added salt).

3. Conclusion

The lability of the Pd–N (aromatic) bond has been extensively exploited in thermodynamically-controlled self-assembly processes to produce elaborated macropolycyclic (cage) structures in water or polar solvents, such as dmso, acetone and MeOH. However, few reports have examined the dynamics of this important coordination bond. The data obtained in the present work are in agreement with those on related compounds, and permit to set the enthalpy of activation for the dissociation of this bond to ≈ 70 kJ mol^{-1}.

4. Experimental section

4.1. General

THF was distilled from sodium/benzophenone. d^6-dmso was dried on 3 Å molecular sieves. 1-(5-Pyrimidinyl)-1-ethanone [6], 1,3,5-tribromomethylbenzene [9], 1,3,5-tribromomethyl-2,4,6-triethylbenzene [10], and [Pd(bipy)(ONO$_2$)$_2$] [11] were synthesized as described in the literature. NMR spectra were recorded with Bruker 500 MHz Avance DRX or 600 MHz Avance II spectrometers.

4.2. 3-(Dimethylamino)-1-(5-pyrimidinyl)-2-propen-1-one (**4**)

A solution of 1-(5-pyrimidinyl)-1-ethanone (0.324 g, 2.65 mmol) in dimethylformamide dimethyl acetal (5 mL, 37 mmol) was refluxed (100 °C) for 2.5 h. Excess of acetal was removed with a rotary evaporator. Sublimation of the residue (35 °C, 0.08 mbar) afforded **4** (0.436 g, 2.46 mmol) in 93% yield, as colored needles, mp 138-139 °C. Elemental analysis calcd (%) for $C_9H_{11}N_3O$ (177.05): C 61.05, H 6.26, N 23.73; found: C 61.34, H 6.50, N 23.70; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 9.25 (s, 1 H, 2-H), 9.15 (s, 2 H, 4- and 6-H), 7.87 (d, $^3J_{H,H} = 12.1$ Hz, 1 H, *H*CN), 5.61 (d, $^3J_{H,H} = 12.1$ Hz, 1 H, *H*CO), 3.20 (s, 3 H, CH_3), 2.97 (s, 3 H, CH_3) ppm; ^{13}C NMR ($CDCl_3$, 126 MHz) δ 183.6 (CO), 159.7, 155.9, 155.0, 132.8, 91.3, 45.3, 37.5 ppm.

4.3. 5-(1H-Pyrazol-3-yl)-pyrimidine (**5**)

A mixture of hydrazine hydrate (0.23 mL, 4.74 mmol) and acetic acid (0.28 mL, 4.84 mmol) in methanol (2 mL) was added drop wise to a solution of **4** (0.420 g, 2.37 mmol) in methanol (8 mL) at 0 °C. As after 5 h stirring at room temperature, traces of **4** were detected, an additional portion of reagents (10% of the initial amount) was added. After 7.5 h, the reaction mixture was diluted with CH_2Cl_2 (80 mL) and stirred with 5% aqueous Na_2CO_3 (20 mL). The aqueous layer was separated and extracted thoroughly with CH_2Cl_2 (40 × 20 mL). The crude product was purified by flash column chromatography (silica, 10% CH_3OH in CH_2Cl_2) to afford **5** (0.320 g, 2.19 mmol) in 92% yield, mp 142-143 °C. Elemental analysis calcd (%) for $C_7H_6N_4$ (146.15): C 57.53, H 4.14, N 38.34; found : C 57.63, H 4.15, N 37.76; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 9.19 (s, 2 H, 4-H and 6-H), 9.08 (s, 1 H, 2-H), 7.79 (s, 1 H, 4′-H or 5′-H), 6.87 (d, $^3J_{H,H}$ = 2.4 Hz, 1 H, 5′-H or 4′-H), 3.31 (s, 1 H, N*H*) ppm; ^{13}C NMR ($CDCl_3$, 126 MHz) δ 157.1 (2-C), 153.9 (4-C and 6-C), 145.4, 130.8, 128.5, 103.1 ppm.

4.4. 1,3,5-Tris [(pyrimidin-5′-yl)-3′-(1′H-pyrazol-1′-yl)methyl] benzene (**1**)

NaH (60% in oil, 0.055 g, 1.375 mmol) was added to a solution of pyrazole **5** (0.150 g, 1.026 mmol) in THF (5 mL) at 0 °C under dinitrogen. After 10 minutes stirring at room temperature a solution of 1,3,5-tribromomethylbenzene (0.117 g, 0.328 mmol) in THF (5 mL) was added to the reaction mixture, which was stirred for 24 h and subsequently quenched by addition of water (5 mL) at 0 °C. The slurry was diluted with water (30 mL) and extracted into CH_2Cl_2 (3 × 20 mL). The crude product was purified by column chromatography (standard alumina, 1% CH_3OH in CH_2Cl_2) to afford tripod **1** (0.101 g, 0.0173 mmol) in 53% yield, based on tribromomethylbenzene, mp 196-197 °C. Elemental analysis calcd (%) for $C_{30}H_{24}N_{12}\cdot CH_3OH$ (584.25): C 63.80, H 4.84, N 28.80; found C 63.44, H 4.40, N 28.96; ^{1}H NMR ($CDCl_3$, 600 MHz, 298 K) δ 9.14 (s, 3 H, 2-H), 9.05 (s, 6 H, 4-H and 6-H), 7.46 (d, $^3J_{H,H}$ = 1.8 Hz, 3 H, 5′-H), 7.03 (s, 3 H, H′), 6.62 (d, $^3J_{H,H}$ = 1.8 Hz, 3 H, 4′-H), 5.34 (s, 6 H, CH_2) ppm; ^{1}H NMR (d^6-dmso, 600 MHz, 298 K) δ 9.07 (s, 3 H, 2-H), 9.06 (s, 6 H, 4-H and 6-H), 7.94 (d, $^3J_{H,H}$ = 2.4 Hz, 3 H, 5′-H), 7.08 (s, 3 H, H′), 6.88 (d, $^3J_{H,H}$ = 2.4 Hz, 3 H, 4′-H), 5.40 (s, 6 H, CH_2) ppm; ^{13}C NMR ($CDCl_3$, 151 MHz, 298 K) δ 157.7 (2-C), 153.7 (4-C and 6-C), 146.0 (3′-C), 138.1 (CH_2C), 131.7 (5′-C), 127.4 (5-C), 126.3 (CH′), 104.0 (4′-C), 55.8 (CH_2) ppm.

4.5. 1,3,5-Tris [(pyrimidin-5′-yl)-3′-(1′H-pyrazol-1′-yl)methyl]-2,4,6-triethylbenzene (**2**)

Prepared as described above for **1** from NaH (60% in oil, 0.10 g, 2.50 mmol), pyrazole **5** (0.300 g, 2.053 mmol) and 1,3,5-tribromomethyl-2,4,6-triethylbenzene (0.290 g, 0.658 mmol). The reaction was quenched after 5 h stirring at room temperature. The crude product was purified by repeated flash column chromatography (silica 35-70 μm, 3-10% gradient CH_3OH in CH_2Cl_2) to afford tripod **4** (0.335 g, 0.519 mmol) in 79% yield, based on tribromomethyltriethylbenzene, mp 147-148 °C. Elemental analysis calcd (%) for $C_{36}H_{36}N_{12}\cdot 0.5\ H_2O$ (645.77) : C 66.96, H 5.77, N 26.03; found C 66.82, H 5.75, N 25.71; ^{1}H NMR ($CDCl_3$, 600 MHz, 298 K) δ 9.13 (s, 3 H, 2-H), 9.10 (s, 6 H, 4-H and 6-H), 7.13 (d, $^3J_{H,H}$ = 2.1 Hz, 3 H, 5′-H), 6.60 (d, $^3J_{H,H}$ = 2.1 Hz, 3 H, 4′-H), 5.53 (s, 6 H, CH_2), 2.81 (q, $^3J_{H,H}$ = 7.7 Hz, 6 H, CH_2'), 1.07 (t, $^3J_{H,H}$ = 7.7 Hz, 9 H, CH_3') ppm; ^{1}H NMR (d^6-dmso, 600 MHz, 298 K) δ 9.14 (s, 6 H, 4-H and 6-H), 9.10 (s, 3 H, 2-H), 7.62 (d, $^3J_{H,H}$ = 2.4 Hz, 3 H, 5′-H), 6.92 (d, $^3J_{H,H}$ = 2.4 Hz, 3 H, 4′-H), 5.51 (s, 6 H, CH_2), 2.86 (q, $^3J_{H,H}$ = 7.5 Hz, 6 H, CH_2'), 0.92 (t, $^3J_{H,H}$ = 7.5 Hz, 9 H, CH_3') ppm; ^{13}C NMR ($CDCl_3$, 151 MHz, 298 K) δ 157.7 (2-C), 153.7 (4- and 6-C), 146.6 (CH_2C and $CH_2'C$), 145.8 (3′-C), 130.2 (5′-C), 127.5 (5-C), 103.5 (4′-C), 50.1 (CH_2), 23.61 (CH_2'), 15.59 (CH_3') ppm.

4.6. [Pd(**1**)(bipy)](NO$_3$)$_2$

A solution of [Pd(bipy)(ONO$_2$)$_2$] (0.0141 g, 3.65 × 10^{-5} mol) in d^6-dmso was added to a suspension of ligand **1** (0.021 g, 3.80 × 10^{-5} mol) in d^6-dmso, the final volume being 1 mL. The resulting clear yellow solution was evaporated to dryness under vacuum at 60 °C. The residue was dissolved in acetone/H_2O. The solid material that precipitated upon further addition of acetone was collected, washed with acetone and dried at 35 °C under vacuum. Yield: 0.0291 g (74%). Elemental analysis calcd (%) for $C_{40}H_{32}N_{16}O_6Pd\cdot 2H_2O\cdot C_3H_6O$ (1033.33) : C 49.98, H 4.10, N 21.69; found C 49.66, H 4.00, N 21.80; ^{1}H NMR (d^6-dmso, 600 MHz, 293 K) δ 10.06 (s, 2 H, 6-H), 9.78 (s, 2 H, 2-H), 9.40 (d, $^4J_{H,H}$ = 1.8 Hz, 2 H, 4-H), 9.16 (s, 2 H, 4°-H, 6°-H), 9.12 (s, 1 H, 2°-H), 8.79 (d, $^3J_{H,H}$ = 7.8 Hz, 2 H, δ-H), 8.52 (ddd, $^3J_{H,H}$ = 7.8 Hz, $^3J_{H,H}$ = 7.8 Hz, $^4J_{H,H}$ = 1.2 Hz, 2 H, γ-H), 8.14 (d, $^4J_{H,H}$ = 1.8 Hz, 2 H, 5′-H), 7.99 (s, 1 H, 5″-H), 7.84 (d, $^3J_{H,H}$ = 5.7 Hz, 2 H, α-H), 7.71 (s, 1 H,

H″), 7.69 (ddd, $^{3}J_{H,H}$ = 7.8 Hz, $^{3}J_{H,H}$ = 5.7 Hz, $^{4}J_{H,H}$ = 1.2 Hz, 2 H, β-H), 7.47 (s, 2 H, H′), 7.02 (d, $^{4}J_{H,H}$ = 1.8 Hz, 2 H, 4′-H), 6.97 (s, 1 H, 4″-H), 5.38 (s, 2 H, CH_2°), 5.37 (AB, J_{AB} = 14.1 Hz, $\Delta\nu_{AB}$ = 115 Hz, 4 H, CH_2) ppm; ^{13}C NMR (d^6-dmso, 151 MHz, 293 K) δ 157.3 (2-C, 2°-C), 156.6 (4-C), 155.7 (ε-C), 153.2 (4°-C, 6°-C), 152.8 (6-C), 151.0 (α-C), 144.9 (3″-C), 143.3 (3′-C), 142.8 (γ-C), 138.0 (C°), 137.4 (C), 132.7 (5′-C, 5″-C), 130.6 (C″), 129.8 (5-C), 128.6 (β-C), 128.3 (C′), 127.0 (5°-C), 124.6 (δ-C), 104.5 (4′-C), 104.0 (4″-C), 55.3 (CH_2), 54.9 (CH_2°) ppm.

4.7. *[Pd(**2**)(bipy)](NO$_3$)$_2$*

A solution of [Pd(bipy)(ONO$_2$)$_2$] (0.0122 g, 3.16×10^{-5} mol) in d^6-dmso was added to a suspension of ligand **2** (0.0202 g, 3.16×10^{-5} mol) in d^6-dmso, the final volume being 1 mL. The resulting clear yellow solution was evaporated to dryness under vacuum at 60 °C. The residue was triturated in acetone/H_2O, and the solvents evaporated to dryness, leaving a pale yellow powder, which was further dried under vacuum at 50 °C. Yield: 0.0302 g (84%). Elemental analysis calcd (%) for $C_{46}H_{44}N_{16}O_6Pd{\cdot}2H_2O{\cdot}C_2H_6OS$ (1137.55) : C 50.68, H 4.78, N 19.70, S 2.82; found C 50.81, H 4.89, N 19.25, S 1.70; ^{1}H NMR (d^6-dmso, 600 MHz, 293 K) δ 9.96 (d, $^{4}J_{H,H}$ = 2.1 Hz, 2 H, 6-H), 9.84 (s, 2 H, 2-H), 9.39 (d, $^{4}J_{H,H}$ = 2.1 Hz, 2 H, 4-H), 9.08 (br s, 1 H, 2°-H), 9.03 (s, 2 H, 4°-H, 6°-H), 8.80 (dd, $^{3}J_{H,H}$ = 7.8 Hz, $^{4}J_{H,H}$ = 1.2 Hz, 2 H, δ-H), 8.51 (ddd, $^{3}J_{H,H}$ = 7.8 Hz, $^{3}J_{H,H}$ = 7.8 Hz, $^{4}J_{H,H}$ = 1.2 Hz, 2 H, γ-H), 8.36 (d, $^{4}J_{H,H}$ = 1.8 Hz, 2 H, 5′-H), 7.73 (d, $^{3}J_{H,H}$ = 2.4 Hz, 1 H, 5″-H), 7.69 (ddd, $^{3}J_{H,H}$ = 7.8 Hz, $^{3}J_{H,H}$ = 5.7 Hz, $^{4}J_{H,H}$ = 1.2 Hz, 2 H, β-H), 7.55 (dd, $^{3}J_{H,H}$ = 5.7 Hz, $^{4}J_{H,H}$ = 1.2 Hz, 2 H, α-H), 7.04 (d, $^{3}J_{H,H}$ = 1.8 Hz, 2 H, 4′-H), 6.87 (d, $^{3}J_{H,H}$ = 1.2 Hz, 1 H, 4″-H), 5.55 (AB, J_{AB} = 15.0 Hz, $\Delta\nu_{AB}$ = 45 Hz, 4 H, CH_2), 5.36 (s, 2 H, CH_2°), 4.18 (q, $^{3}J_{H,H}$ = 7.8 Hz, 2 H, CH_2″), 2.98 (m, 4 H, CH_2′), 1.33 (t, $^{3}J_{H,H}$ = 7.8 Hz, 3 H, CH_3″), 0.78 (t, $^{3}J_{H,H}$ = 7.2 Hz, 3 H, CH_3′) ppm; ^{13}C NMR (d^6-dmso, 151 MHz, 293 K) δ 157.4 (2-C), 157.2 (2°-C), 156.9 (4-C), 155.6 (ε-C), 153.5 (6-C), 153.0 (4°-C, 6°-C), 150.5 (α-C), 147.0 (C″), 144.9 (C′), 144.3 (3″-C), 143.1 (3′-C), 142.9 (γ-C), 134.0 (5′-C), 132.1 (5″-C), 131.3 (C), 130.3 (5-C), 129.9 (C°), 128.8 (β-C), 127.0 (5°-C), 124.7 (δ-C), 103.8 (4′-C), 103.5 (4″-C), 49.0 (CH_2, CH_2°), 23.9 (CH_2″), 22.2 (CH_2′), 15.8 (CH_3″), 15.7 (CH_3′) ppm.

5. Conflicts of interest

There is no conflict of interest affecting the corresponding authors and his co-authors.

Acknowledgments

The French Ministry of Higher Education and Research is thanked for a postdoctoral fellowship to PPM. Dr. Michel Meyer is gratefully acknowledged for helpful discussions.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.crci.2009.03.002.

References

[1] (a) M. Fujita, M. Tominaga, A. Hori, B. Therrien, Acc. Chem. Res. 38 (2005) 371 ;
(b) M. Aoyagi, K. Biradha, M. Fujita, J. Am. Chem. Soc. 121 (1999) 7457 ;
(c) S. Hiraoka, M. Fujita, J. Am. Chem. Soc. 121 (1999) 10239 ;
(d) M. Yoshizawa, Y. Takeyama, T. Okano, M. Fujita, J. Am. Chem. Soc. 125 (2003) 3243 ;
(e) T. Yamaguchi, M. Fujita, Angew. Chem. Int. Ed. 47 (2008) 2067 ;
(f) M. Yoshizawa, K. Kumazawa, M. Fujita, J. Am. Chem. Soc. 127 (2005) 13456 ;
(g) D.K. Chand, R. Manivannan, H.S. Sahoo, K. Jeyakumar, Eur. J. Inorg. Chem. (2005) 3346.

[2] (a) F.G.M. Niele, R.J.M. Nolte, J. Am. Chem. Soc. 110 (1988) 172 ;
(b) S.J. Park, J.W. Lee, S. Sakamoto, K. Yamaguchi, J.I. Hong, Chem. Eur. J. 9 (2003) 1768 ;
(c) S. Tashiro, M. Tominaga, T. Kusukawa, M. Kawano, S. Sakamoto, K. Yamaguchi, M. Fujita, Angew. Chem. Int. Ed. 42 (2003) 3267.

[3] (a) N. Takeda, K. Umemoto, K. Yamaguchi, M. Fujita, Nature 398 (1999) 794 ;
(b) K. Umemoto, K. Yamaguchi, M. Fujita, J. Am. Chem. Soc. 122 (2000) 7150 ;
(c) K. Umemoto, H. Tsukui, T. Kusukawa, K. Biradha, M. Fujita, Angew. Chem. Int. Ed. 40 (2001) 2620 ;
(d) M. Tadokoro, S. Mizugaki, M. Kozaki, K. Okada, Chem. Commun. (Camb.) (2005) 1140 ;
(e) E. Barea, J.A.R. Navarro, J.M. Salas, M. Quirós, M. Willermann, B. Lippert, Chem. Eur. J. 9 (2003) 4414 ;
(f) J.P. Bourgeois, M. Fujita, M. Kawano, S. Sakamoto, K. Yamaguchi, J. Am. Chem. Soc. 125 (2003) 9260 ;
(g) Y. Miura, M. Nanjo, K. Mochida, T. Iwamoto, M. Kira, Inorg. Chem. Commun. 7 (2004) 1017.

[4] S.Y. Jong, J. Kim, M. Kim, S.H. Park, W.S. Jeon, J. Heo, K. Kim, Angew. Chem. Int. Ed. 40 (2001) 2116.

[5] A. Tanaka, T. Terasawa, H. Hagihara, Y. Sakuma, N. Ishibe, M. Sawada, H. Takasugi, H. Tanaka, J. Med. Chem. 41 (1998) 2390.

[6] (a) M.H. Jung, J.G. Park, K.J. Yang, M.J. Lee, Arch. Pharm. Pharm. Med. Chem. 334 (2001) 79 ;
(b) T. Rho, Y.F. Abuh, Synth. Commun. 24 (1994) 253.

[7] A.L. Gérard, A. Bouillon, C. Mahatsekake, V. Collot, S. Rault, Tetrahedron Lett. 47 (2006) 4665.

[8] J. Chin, C. Walsdorff, B. Stranix, J. Oh, H.J. Chung, S.M. Park, K. Kim, Angew. Chem. Int. Ed. 38 (1999) 2756.
[9] (a) W.P. Cochrane, P.L. Pauson, T.S. Sevens, J. Chem. Soc. (C) (1968) 630 ;
(b) E. Díez-Barra, J.C. García-Martínez, S. Merino, R. del Rey, J. Rodríguez-López, P. Sánchez-Verdú, J. Tejeda, J. Org. Chem. 66 (2001) 5664.
[10] C. Walsdorff, W. Saak, S. Pohl, J. Chem. Res. (1996) 1601.
[11] S. Wimmer, P. Castan, F.L. Wimmer, N.P. Johnson, J. Chem. Soc., Dalton Trans. (1989) 403.
[12] (a) E.W. Abel, A. Gelling, K.G. Orrell, A.G. Osborne, V. Sik, Chem. Commun. (1996) 2329 ;
(b) A. Gelling, M.D. Olsen, K.G. Orrell, A.G. Osborne, V. Sik, Chem. Commun. (1997) 587 ;
(c) A. Gelling, M.D. Olsen, K.G. Orrell, A.G. Osborne, V. Sik, Inorg. Chim. Acta. 264 (1997) 257 ;
(d) F. Gómez-de la Torre, A. de la Hoz, F.A. Jalón, B.R. Manzano, A. Otero, A.M. Rodríguez, M.C. Rodríguez-Pérez, Inorg. Chem. 37 (1998) 6606.