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Note

Synthesis, crystal structure and VT-NMR study of *cis*-[$PdCl_2(CNC_6H_3Me_2$-2,6)(PPh_3)]

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ABSTRACT

The complex *cis*-[$PdCl_2(CNC_6H_3Me_2$-2,6)(PPh_3)] has been prepared and fully characterized. Its crystal structure has been determined showing the chloro ligands in *cis*-disposition. A VT-NMR study shows this complex to be in equilibrium with *trans*-[$PdCl_2(PPh_3)_2$] and *cis*-[$PdCl_2(CNC_6H_3Me_2$-2,6$)_2$]. The equilibrium is fast at room temperature but at −50 °C all three species are observed in solution in 10:1:1 M ratio. The activation parameters for this equilibrium have been calculated.

1. Introduction

Compounds of the type [$PdCl_2$(isocyanide)(phosphine)] are rather scarce and only a few of them have been fully characterized including their crystal structures [1–5]. As far as we are aware, all of them are of *cis*-geometry with the only exception of *trans*-[$PdCl_2(CN^{sec}Bu)${PPh(α-naphthyl)(C_6H_4R-4)}] (R = Ph, OMe) [6], attributable to the mutual repulsion of the sterically demanding neutral ligands if they were in *cis* position. They have been prepared by rather inefficient, multistep methods, namely (i) by reacting complexes of the types [$PdCl_2(PR_3)_2$] [7], [$PdCl(\mu$-Cl)$(PR_3)]_2$ [1] or [$PdCl_2$(P^N)] (P^N = chelating imine–phosphine [3] or imino-phosphorane-phosphine [5]) with isocyanide; (ii) by reacting complexes *cis*-[$PdCl_2(CNR)_2$] with phosphine [6,8] (some of these reactions have been used to resolve racemic tertiary phosphines); [6] (iii) by reacting [$PdCl_2(CNR)_2$] with rhodium or palladium complexes of the types [RhCl(cod)(P^N)] [9,10], [Rh(η^5-C_5Me_5)(P^N′)$C1_2$] [11], (cod = 1,5-cyclooctadiene, P^N = PPh_2(2-pyOMe-6)), or [Pd{CH_2C(Me)CH_2}(P^N′)] (P^N′ = PPh_2(2-py)) [4]. The reactivity of these complexes towards amines [12,13] nitrilimines [14], nitrilylides [15], etc., has been explored leading to the synthesis of a variety of cyclic carbene complexes.

Although *cis*-[$PdCl_2$(CNXy)(PPh_3)] (**1**, Xy = Xylyl = $C_6H_3Me_2$-2,6) had been previously prepared from *cis*-[$PdCl_2(CNXy)_2$] and PPh_3 [16], it was only characterized by its melting point and IR spectrum [17]. We report here the one-pot, 100% atom-efficient synthesis of **1** from equimolar amounts of $PdCl_2$, XyNC and PPh_3 (Scheme 1) and its variable temperature (VT) ^{1}H, ^{13}C and ^{31}P NMR spectra showing it to be in equilibrium with *cis*-[$PdCl_2(CNXy)_2$] (**2**) and *trans*-[$PdCl_2(PPh_3)_2$] (**3**).

As far as we are aware, rearrangement equilibria of the type described in this paper, 2·**1** ⇆ **2** + **3**, is unprecedented for these mixed ligand complexes.

2. Experimental

2.1. Materials

Acetone, Et_2O and CH_2Cl_2 were distilled before use, from $KMnO_4$, Na/benzofenone and CaH_2, respectively. $CHCl_3$ (Baker), $CDCl_3$ (SDS) and the reagents $PdCl_2$ (Johnson Matthey), XyNC and PPh_3 (Fluka) were used as purchased.

2.2. Physical measurements

Elemental analyses of carbon, hydrogen and nitrogen were carried out with a Carlo Erba 1106 microanalyzer. The melting point was determined on a Reichert apparatus and is uncorrected. The IR spectrum was recorded on a Perkin-Elmer 16F PC FT-IR spectrometer in the range of 4000–200 cm^{-1} region, with Nujol mulls between polyethylene sheets. The NMR spectra were recorded in a Bruker Avance 400 NMR spectrometer, every 10 °C in the range of 25 to −50 °C using $CDCl_3$ solutions. Chemical shifts are referenced to TMS (^{1}H and ^{13}C{^{1}H}) and H_3PO_4 (^{31}P{^{1}H}). The NMR assignments were performed with the help of APT, HMQC and HMBC experiments.

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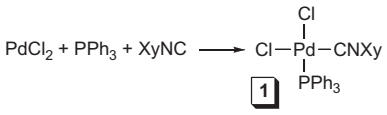


Scheme 1. Synthesis of complex **1** from $PdCl_2$, PPh_3 and XyNC.

2.3. Synthesis of cis-[$PdCl_2$(CNXy)(PPh_3)] (**1**) and VT ^{1}H and ^{31}P NMR study of the equilibrium. 2·cis-[$PdCl_2$(CNXy)(PPh_3)] ⇆ cis-[$PdCl_2$(CNXy)$_2$] + trans-[$PdCl_2$(PPh_3)$_2$]

To a suspension of $PdCl_2$ (162.5 mg, 1.39 mmol) in acetone (20 mL) were successively added XyNC (182 mg, 1.39 mmol) and PPh_3 (364 mg, 1.39 mmol). After 1 h of stirring, the resulting greenish-yellow suspension was filtered. The solid collected was dissolved in $CHCl_3$ (10 mL), filtered through a short pad of Celite, concentrated under vacuum (5 mL), and Et_2O (25 mL) was added. The suspension was filtered and the solid collected was dried, first by suction and then in an oven at 70 °C for 7 h, to give *cis*-[$PdCl_2$(PPh_3)(CNXy)] (**1**) as a pale yellow solid. Yield: 542 mg, 0.95 mmol, 70%. Mp: 232 °C (dec). IR (Nujol, cm^{-1}): ν(C≡N) 2206 (strong), ν(Pd–Cl) 347 (medium), 298 (strong). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ 1.95 (s, 6H, Me), 6.98 (d, 2H, $^3J_{HH}$ = 7.6 Hz, *meta*-Xy), 7.18 (t, 1H, $^3J_{HH}$ = 7.6 Hz, *para*-Xy), 7.35–7.50 (various m, 9 H, PPh_3), 7.72 ("d", 6H, *ortho*-PPh_3, $^3J_{HH}$ = 7.2 Hz). ^{1}H NMR (400 MHz, $CDCl_3$, −50 °C, TMS): *cis*-[$PdCl_2$(CNXy)(PPh_3)] (**1**, 71.4%) δ: 1.97 (s, 6H, Me), 7.03 (d, 2H, $^3J_{HH}$ = 7.6 Hz, *meta*-Xy), 7.23 (t, 1H, $^3J_{HH}$ = 7.6 Hz, *para*-Xy, overlapped with *para*-Xy of complex **2**), 7.46–7.55 (various m, 9H, *meta*- + *para*-PPh_3, overlapped with the homologous resonances in **3**), 7.78 (dd, 6H, *ortho*-PPh_3, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 4.8 Hz); *cis*-[$PdCl_2$(CNXy)$_2$] (**2**, 14.3%): 1.65 (s, 3H, Me), 6.95 (d, 2H, *meta*-Xy, $^3J_{HH}$ = 7.6 Hz), 7.20 (t, 1H, *para*-Xy, $^3J_{HH}$ = 7.6 Hz, overlapped with *para*-Xy of complex **1**); *trans*-[$PdCl_2$(PPh_3)$_2$] (**3**, 14.3%): 7.46–7.55 (various m, 9H, *meta*- + *para*-PPh_3, overlapped with the homologous resonances in **1**), 7.69 (m, 6H, *ortho*-PPh_3). ^{13}C{^{1}H} APT NMR (100.8 MHz, $CDCl_3$, 25 °C, TMS): δ 18.2 (Me), 127.9 (*meta*-Xy), 128.8 (br s, *meta*-Ph, PPh_3), 130.3 (*para*-Xy), 131.8 (br s, *para*-Ph, PPh_3), 134.4 (br s, *ortho*-Ph, PPh_3), 135.6 (*ortho*-Xy). Pd–*C*NXy and *ipso*-Ph(PPh_3) not observed. ^{13}C{^{1}H} APT NMR (100.8 MHz, $CDCl_3$, −50 °C, TMS): *cis*-[$PdCl_2$(CNXy)(PPh_3)] (**1**) δ: 18.1 (Me), 124.5 (Pd–CN), 127.7 (*meta*-Xy, coincident with *meta*-Xy for complex **2**), 128.0 (d, *ipso*-PPh_3, J_{CP} = 58.5 Hz), 128.6 (d, *meta*-PPh_3, J_{CP} = 12 Hz), 130.3 (*para*-Xy), 131.9 (d, *para*-PPh_3, J_{CP} = 2 Hz), 134.0 (d, *ortho*-PPh_3, J_{CP} = 11.0 Hz), 135.4 (*ortho*-Xy); *cis*-[$PdCl_2$(CNXy)$_2$] (**2**): δ 17.8 (Me), 123.3 (Pd–*C*NXy), 127.7 (*meta*-Xy, coincident with *meta*-Xy for complex **1**), 130.9 (*para*-Xy), 134.3 (*ortho*-Xy); *trans*-[$PdCl_2$(PPh_3)$_2$] (**3**): δ 126.8 ("t", *ipso*-PPh_3, N = 54.0 Hz), 129.0 ("t", *meta*-PPh_3, N = 11 Hz), 132.1 (s, *para*-PPh_3), 133.7 ("t", *ortho*-PPh_3, N = 12 Hz). ^{31}P{^{1}H} NMR (162.3 MHz, $CDCl_3$, 25 °C): δ 26.2 (v br s). ^{31}P{^{1}H} NMR (162.3 MHz, $CDCl_3$, −50 °C): *cis*-[$PdCl_2$(CNXy)(PPh_3)] (**1**): δ 29.3; *trans*-[$PdCl_2$(PPh_3)$_2$] (**3**): δ 22.8.

Crystals of **1** suitable for an X-ray diffraction study grew at 4 °C after layering Et_2O over a CH_2Cl_2 solution containing an equimolar mixture of $PdCl_2$, PPh_3 and XyNC. After drying the crystals in an oven at 70 °C for 7 h, the melting point and IR spectrum coincided with those of the crude material.

2.4. X-ray crystallography

Complex **1** was measured on a Bruker Smart APEX machine. Data were collected using monochromated Mo Kα radiation. The structure was solved by direct methods. It was refined anisotropically on F^2. The methyl groups were refined using rigid groups, and the other hydrogen atoms were refined using a riding model. Details of the crystal data and structure refinement of the complex are listed in Table 1.

3. Results and discussion

3.1. Synthetic aspects and general properties

The method here described for the synthesis of complex **1**, from equimolar amounts of $PdCl_2$, XyNC and PPh_3 (Scheme 1) is more straightforward and atom-efficient than any of those previously described for complexes of this type, some of them being rather cumbersome. In fact, with respect to the more efficient ones, [$PdCl_2$(CNR)$_2$] + phosphine or [$PdCl_2$(phosphine)$_2$] + RNC, our method not only avoids one step but also saves one equivalent of isocyanide or phosphine, respectively.

When we did the reaction in acetone, **1** precipitated from the reaction mixture and was isolated in 70% yield after recrystallization from $CHCl_3/Et_2O$, which was necessary in order to separate a small amount of $PdCl_2$. In spite of the fact that the variable temperature NMR study described below proves that an equilibrium exists in $CDCl_3$ solution between the mixed ligand complex **1**, *cis*-[$PdCl_2$(CNXy)$_2$] (**2**) and *trans*-[$PdCl_2$(PPh_3)$_2$] (**3**), the procedure described in Section 2 leads to the precipitation of pure **1**, as shown by the coincidence of its melting point and IR spectrum with those previously reported [18], and also with those obtained from a crop of single crystals that we dried in an oven at 70 °C for 7 h (margin of error: ΔMp, 3 °C; Δν, 3 cm^{-1}). The purity of the isolated complex **1** could be attributed to the fact that **1** is the major species in the reaction mixture (**1**:**2**:**3** = 10:1:1 in $CDCl_3$ at −50 °C) and/or to differences in solubility. In fact, **1** was the only species that crystallized when Et_2O was layered over a solution of the reaction mixture in CH_2Cl_2.

3.2. Structure description

The crystal structure of **1** (Fig. 1 and Table 1) shows the palladium atom in a slightly distorted square planar environment, coordinated to a PPh_3, a XyNC and two chloro ligands in mutually *cis*-disposition. The bond distances and angles are similar to those

Table 1
Crystal data and structure refinement of complex **1**.

Formula	$C_{27}H_{24}Cl_2NPPd$
Formula weight	570.74
T (K)	100(2)
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	9.8101(6)
b (Å)	11.8776(7)
c (Å)	12.0372(7)
α (°)	87.239(2)
β (°)	67.363(2)
γ (°)	78.693(2)
V (Å^3)	1268.82(13)
Z	2
ρ_{calcd} (Mg m^{-3})	1.494
μ (Mo Kα) (mm^{-1})	1.020
F(000)	576
Crystal size (mm)	0.14 × 0.09 × 0.02
θ (°)	1.83–28.18
Number of reflections collected	14774
Number of independent reflections (R_{int})	5704 (0.0316)
Transmission	0.9799–0.8555
Restraints/parameters	0/291
Goodness-of-fit (GOF) on F^2	1.057
R_1 ($I > 2\sigma(I)$)	0.0373
wR_2 (all reflections)	0.0820
Largest difference in peak and hole (e Å^{-3})	0.802/−0.526

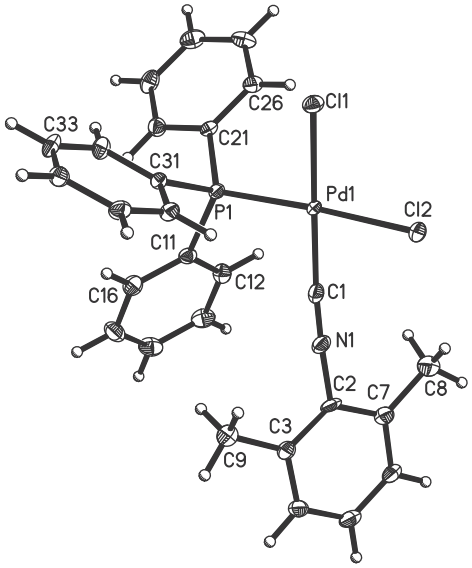


Fig. 1. Crystal structure of complex **1**. Thermal ellipsoid representation plot (50% probability) of complex **1**. Selected bond lengths (Å) and angles (°): Pd(1)–C(1) 1.916(3), Pd(1)–P(1) 2.2607(7), Pd(1)–Cl(1) 2.3079(7), Pd(1)–Cl(2) 2.3463(7), C(1)–N(1) 1.152(4). C(1)–Pd(1)–P(1) 93.58(8), P(1)–Pd(1)–Cl(1) 88.86(3), C(1)–Pd(1)–Cl(2) 84.08(9), Cl(1)–Pd(1)–Cl(2) 93.29(3), N(1)–C(1)–Pd(1) 173.7(3).

found in the few other palladium complexes of this type characterized by their crystal structures [1–5]. The different Pd–Cl bond distances, Pd(1)–Cl(1) 2.3079(7), Pd(1)–Cl(2) 2.3463(7) found in **1**, and also in its homologous complexes, account for the greater *trans* influence of phosphines with respect to isocyanides.

Non-classical hydrogen bonds of the type C–H···Cl form in which two C–H groups, each of them on one phenyl ring of the same molecule, connect the chloro ligands of two other molecules, giving rise to a double zig-zag chain along the *b* axis (Fig. 2).

3.3. VT-NMR studies

3.3.1. The 2·**1** ⇆ **2** + **3** equilibrium

At room temperature, the ^{1}H NMR spectrum of **1** showed the expected resonances. However, a very broad signal in the ^{31}P NMR spectrum, along with the fact that ^{13}C APT spectrum did not show the *ipso*-C resonance for the PPh_3 ligand and the remaining phosphine nuclei gave broad resonances instead of the expected doublets, suggested to us that a dynamic process could be occurring in solution that we decided to investigate by means of a variable temperature NMR study.

We show below VT ^{1}H and ^{31}P NMR spectra measured, every 10 °C, in the ranges of 25 to −50 °C (^{1}H, Fig. 3) or 25 to −20 °C (^{31}P, Fig. 4), respectively. Fig. 3 shows, for instance, that the ^{1}H NMR resonances appearing at room temperature at 1.95 (Me) and 6.98 (*meta*-Xy) ppm, coalesce at −5 and −15 °C, respectively, and each of them clearly splits, at −50 °C into two resonances at 1.97 and 1.65 (Me) or at 6.95 and 7.03 (*meta*-Xy) ppm, with 1:5 intensities ratio in both cases. We assigned the resonances at 1.65 and 6.95 to complex **2**, based on the spectrum of a pure sample of this complex measured at −50 °C, which means that the more intense resonances at 1.97 and 7.03 ppm correspond to complex **1** and that the **1**:**2** M ratio is 10. Similarly, the doublet at 7.72 ppm in the room temperature NMR spectrum, assigned to the *ortho*-PPh_3 protons, coalesces at around −10 °C and splits at −50 °C into a doublet of doublets and an apparent quartet centred at 7.78 and 7.69 ppm, respectively, with 5:1 intensities ratio. In turn, the very broad resonance appearing in the room temperature ^{31}P NMR spectrum at around 26 ppm, splits below 15 °C into two

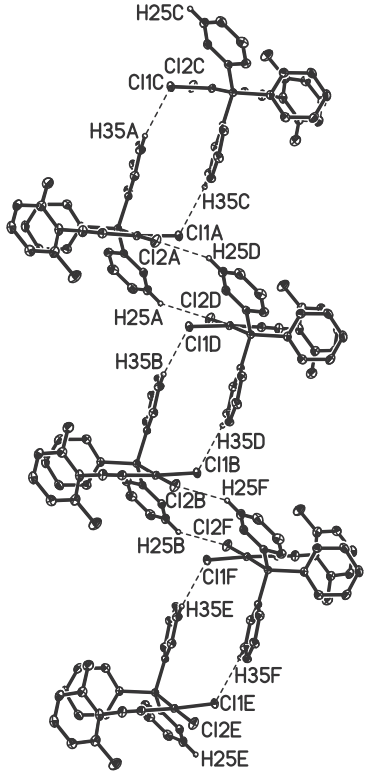


Fig. 2. Double zig-zag chain along the *b* axis in **1** resulting from C–H···Cl hydrogen bonds. Bond distances (Å) and angles (°): H(25)···Cl(2)#1, 2.77; C(25)···Cl(2)#1, 3.603; H(35)···Cl(1)#2, 2.73; C(35)···Cl(1)#2, 3.519; C(25)–H(25)–Cl(2)#1, 146.8; C(35)–H(35)–Cl(1)#2, 141.2.

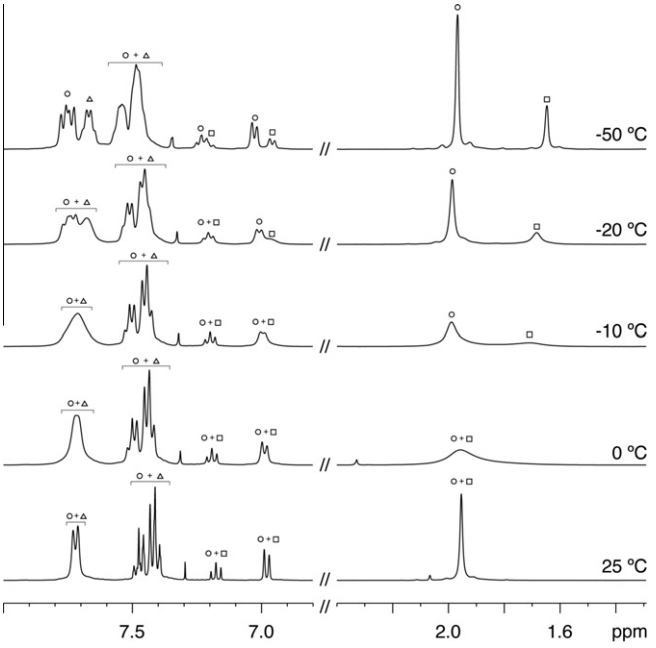


Fig. 3. VT ^{1}H NMR spectra (400 MHz, $CDCl_3$) showing the resonances of complexes *cis*-[$PdCl_2$(CNXy)(PPh_3)] (**1**, circle), *cis*-[$PdCl_2$(CNXy)$_2$] (**2**, square) and *trans*-[$PdCl_2$(PPh_3)$_2$] (**3**, triangle).

resonances (22.8 and 29.3 ppm at −20 °C) with 1:5 intensities ratio (Fig. 4). We attribute them to complexes **3** and **1**, respectively, based on the ^{31}P NMR spectrum of a pure sample of **3** measured at the same temperatures. The same behaviour can be deduced

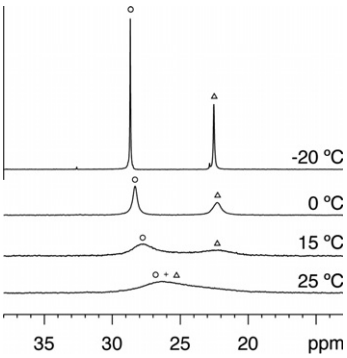
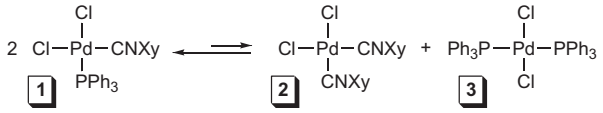


Fig. 4. VT ^{31}P NMR spectra (162.3 MHz, $CDCl_3$) showing the resonances of *cis*-$[PdCl_2(CNXy)(PPh_3)]$ (**1**, circle) and *trans*-$[PdCl_2(PPh_3)_2]$ (**3**, triangle).



Scheme 2. Equilibrium between **1**, **2** and **3**.

from the ^{13}C APT NMR spectra measured at 25 and −50 °C (see Fig. S1, Supporting information). These data prove that an equilibrium exists in $CDCl_3$ solution between complexes **1**, **2** and **3** (Scheme 2). Its composition depends on the temperature and, at −50 °C, is 10:1:1. The equilibrium is fast at room temperature and the NMR spectra show the average resonances which, as expected, are closer to those of the most abundant species **1**.

In support of the above conclusions is the fact that a $CDCl_3$ solution containing equimolar amounts of independently prepared *cis*-$[PdCl_2(CNXy)_2]$ (**2**) and *trans*-$[PdCl_2(PPh_3)_2]$ (**3**) gave, at each temperature, identical ^1H, ^{13}C and ^{31}P NMR spectra as those described above.

*3.3.2. Activation parameters for the 2·**1** ⇆ **2** + **3** equilibrium*

Line shape analyses of both the Me (^1H, 223–298 K) and the PPh_3 (^{31}P, 223–253 K) resonances allowed us to determine a series of rate constants (k) at different temperatures. Although the broadness of the ^{31}P resonances in the 253–298 K range led to unacceptable errors, the k values simulated from ^{31}P between 223 and 253 K are in agreement with those obtained from the ^1H methyl resonances in the whole 223–298 K range thus confirming of each of the three species, **1**, **2** and **3**, is involved only in the equilibrium 2·**1** ⇆ **2** + **3** which is probably a sum of more simple equilibria. The activation parameteres for this overall equilibrium could be calculated from the rate constants by use of the Arrhenius (empirical activation energy, $E_a = 109 \pm 2$ kJ mol^{-1}) and Eyring (activation enthalpy, $\Delta H^{\neq} = 107 \pm 4$ kJ mol^{-1}; and entropy, $\Delta S^{\neq} = 199 \pm 9$ J K^{-1} mol^{-1}) equations. From these data, the activation free energy can be calculated for a given temperature (at 298 K, $\Delta G^{\neq}_{298K} = 48 \pm 1$ kJ mol^{-1}, for details see Supplementary material). We have not found in the literature any data to which our values could be compared. Although it is likely that the process we are studying differ in many respects from common substitution reactions, the high positive value found for the activation entropy is still surprising and suggests that a dissociative process is the rate limiting step in the overall process, even though the formation of a chloro-bridged dinuclear intermediate can not be ruled out. Since, in the absence on an added ligand, dissociation of **1** is necessary in order to provide the PPh_3 and XyNC ligands responsible for the nucleophilic attacks leading to **2** and **3**, the robustness of the Pd–PPh_3 and Pd–CNXy bonds could account for the $\Delta S^{\neq}$ value found.

4. Conclusion

We describe a highly atom-efficient, one-pot synthesis of complex *cis*-$[PdCl_2(CNXy)(PPh_3)]$ and the equilibrium in solution between this complex, *cis*-$[PdCl_2(CNXy)_2]$ and *trans*-$[PdCl_2(PPh_3)_2]$ which is unprecedented for this type of complexes.

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Appendix A. Supplementary material

CCDC 827505 contains the supplementary crystallographic data for complex **1**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. The Supplementary material includes also the checkcif for complex **1**, the $^{13}C\{^1H\}$ APT NMR spectra showing the resonances in the equilibrium 2·**1** ⇆ **2** + **3** at 25 and at −50 °C and a VT NMR study allowing the determination of the rate constants and activation parameters for this equilibrium. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.11.038.

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