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# Pentynol to furan conversion – Search for the best *trans*-$[MX_2(YNC_{10}H_{14}O)_2]$ catalyst

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ABSTRACT

Conversion of 4-pentyn-1-ol (**A**) into 2-methyl-2-pent-4-ynyloxy-tetrahydrofuran (**B**) is catalysed by camphorimine complexes *trans*-$[PdCl_2(YNC_{10}H_{14}O)_2]$ (Y = $NMe_2$, NHMe, $NH_2$, OH, OMe, $Pr^i$, Ph), *trans*-$[PdBr_2(YNC_{10}H_{14}O)_2]$ (Y = $NMe_2$, $NH_2$, OH, Ph), *trans*-$[PtCl_2(YNC_{10}H_{14}O)_2]$ (Y = $NMe_2$, NHMe, $NH_2$). In the presence of $H_2O$ those catalysts further promote the conversion of 2-methyl-2-pent-4-ynyloxy-tetrahydrofuran (**B**) into 5-(2-methyl-tetrahydrofuran-2-yloxy)-pentan-2-one (**C**). The efficiency of each process highly depends on the characteristics of the Y group (at the camphor ligand), the halide (co-ligand) and the transition metal. To ascertain on the relevance of each parameter into the properties of the catalysts, the rate constants for A → B and B → C processes, TON, TOF and catalysts Activities ($A_i$) for A → B conversion were calculated. From the three sets of complexes studied the most efficient catalyst is *trans*-$[PdCl_2(H_2NNC_{10}H_{14}O)_2]$ while *trans*-$[PdCl_2(PhNC_{10}H_{14}O)_2]$ is the less efficient. Palladium chloride are considerably better catalysts than palladium bromide complexes except in the case of *trans*-$[PdBr_2(HONC_{10}H_{14}O)_2]$ that resembles chloride complexes efficiency. Compared to palladium, platinum complexes are considerably less efficient catalysts.



## 1. Introduction

Within our study of C≡C bond activation we found that *trans*-$[PdCl_2(Me_2NNC_{10}H_{14}O)_2]$ was an efficient catalyst for C–C or C–O bond formation from alkynes or alkynols leading respectively to aromatic (P1) or heterocyclic species (P2) (Scheme 1) [1,2]. The high selectivity of *trans*-$[PdCl_2(Me_2NNC_{10}H_{14}O)_2]$ for activation of alkyne triple bonds affording 1,3,5 benzenes (P1) or furan type species (P2) was a challenge to get an insight in the activity of related camphor catalysts and try to rationalize the aspects that drive their activity in order to find the best catalyst.

Three sets of camphorimine complexes *trans*-$[MX_2(YNC_{10}H_{14}O)_2]$ were synthesized and their efficiency to catalyze the formation of 2-methyl-2-pent-4-ynyloxy-tetrahydrofuran (**B**) from 4-pentyn-1-ol was evaluated aiming to ascertain on the effect of the camphorimine group (Y), the halide co-ligand (X) and the metal (M) in the process.

The search for high efficient and selective catalysts for the synthesis of aromatic or heterocyclic organic compounds, including biologically active species or materials [3–10] in particular through processes that contribute to atom economy and/or less residues are actual targets for synthetic chemistry.

In this work we address the topic of efficiency by controlling the characteristics of the camphorimine Y group and reaction time in a process with atom economy of 100%.

## 2. Results and discussion

In chlorinated solvents (chloroform or dichloromethane) at room temperature complexes *trans*-$[MX_2L_2]$ (M = Pd or Pt; X = Cl or Br; L = camphorimine) promote the cycloisomerization molecule of 4-pentyn-1-ol (**A**) with concomitant addition of one molecule 4-pentyn-1-ol affording 2-methyl-2-pent-4-ynyloxy-tetrahydrofuran (**B**). In $CDCl_3$ (*ca.* 3 mL) using as catalyst *trans*-$[PdCl_2(Me_2NNC_{10}H_{14}O)_2]$ (*ca.* 2%) the maximum conversion of **A** (50 μL) into **B** is achieved in 2 h (see Section 4 for further details). After that, the hydration of B affording 5-(2-methyl-tetrahydrofuran-2-yloxy)-pentan-2-one (**C**) becomes a competitive process precluding higher yields of **B**. This hydration process is triggered even by traces of water in 4-pentyn-ol, a fact that is undesired under organic synthetic purposes. Addition of $H_2O$ enables the formation of **C** and prompts hydrolysis to 5-hydroxy-2-pentanone (**D**) (Scheme 2).

Former studies [1,2] suggested that the Y groups at the camphor ligand ($YNC_{10}H_{14}O$) play a significant role in the catalytic properties of the complexes either for cyclotrimerization or heterocycle formation. In order to search for the best catalyst we decided to prepare several camphor palladium complexes

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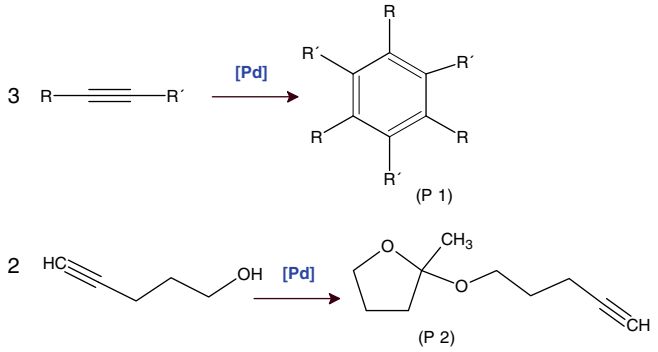



**Scheme 1.**

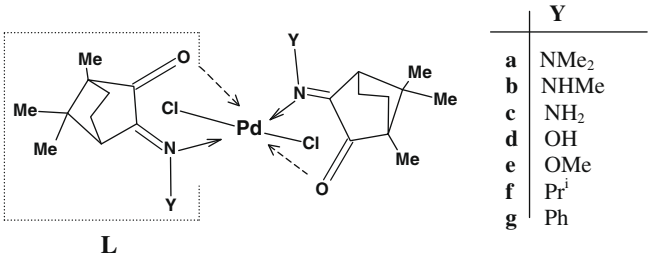



**Fig. 1.** Schematic representation of *trans*-$[PdCl_2(YNC_{10}H_{14}O)_2]$.

*trans*-$[PdCl_2(YNC_{10}H_{14}O)_2]$ (Y = $NMe_2$, **1a**; NHMe, **1b**; $NH_2$, **1c**; OH, **1d**; OMe, **1e**; $Pr^i$, **1f**; Ph, **1g**) (Eq. (1), Fig. 1) and evaluate their ability to promote A → B conversion and reduce **C** formation.

$$PdCl_2 + 2YNC_{10}H_{14}O \rightarrow \textit{trans}\text{-}[PdCl_2(YNC_{10}H_{14}O)_2] \quad (1)$$

The formation of **B** and **C** (Scheme 2) were monitored by NMR ($^1H$ and $^{13}C$) and the signals assigned to the methyl groups **B** (1.34) and **C** (1.32) were integrated and the values plotted against time. Fig. 2 displays spectra obtained in the reaction of 4-pentyn-1-ol with *trans*-$[PdCl_2(Me_2NNC_{10}H_{14}O)_2]$.

The reactions were followed for at least one week, although the maximum conversion in B was achieved in 2 h (Table 1), except for *trans*-$[PdCl_2(YNC_{10}H_{14}O)_2]$ (Y = Ph or $Pr^i$).

The rate constants were calculated considering that coordination of 4-pentyn-1-ol to the metal site is accompanied by ligand release. This assumption is supported by the fact that addition of free ligand ($YNC_{10}H_{14}O$) to the reaction mixture strongly inhibits formation of **B** and **C**. To account for this a pre-equilibrium step (see Section 4 for a scheme) was considered and its constant included in the kinetic fittings, that must be regarded as apparent kinetic constants ($k_1$ and $k_2$) (Table 1).

Fittings and experimental data correlate by factors not lower than 98% (Fig. 3).

The rate constants show that the reactivity follows the order of Y basicity, i.e $NH_2 \approx OH > NMe_2 > NHMe > NOMe > Pr^i > Ph$. *trans*-$[PdCl_2(PhNC_{10}H_{14}O)_2]$ with a poor basic Y group displays no higher catalytic activity than $PdCl_2$ [2].

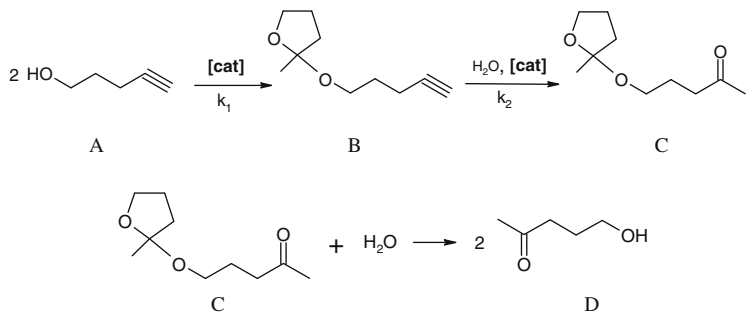
The presence of a base ($Et_3N$ [11]) or THF, [12] was previously mentioned to enable the catalytic cycloisomerization of 4-pentyn-1ol. Using *trans*-$[PdCl_2(YNC_{10}H_{14}O)_2]$ as catalysts neither a base nor a basic solvent is necessary since the camphor ligands play that role through the Y group. In fact, the poorest catalyst (Y = Ph) is that with less basic Y group. In addition, the Y group also stabilizes the alcohol group of 4-pentyn-1-ol inhibiting ready cyclization to a vinylidene type species observed in the cycloisomerization of 4-pentyn-1-ol promoted by Mo or W carbonyl catalysts [4,11–15]. No such vinylidene type species was detected in processes catalysed by camphorimine catalysts.

Compared to *trans*-$[PdCl_2(YNC_{10}H_{14}O)_2$ (Y = $NMe_2$, $NH_2$) the kinetic constants calculated for *trans*-$[PdCl_2(MeHNNC_{10}H_{14}O)_2]$ are unexpectedly low (three orders of magnitude, Table 1). This behaviour can be rationalized based on former studies [16] that showed that the camphorimine (Y = MeH) $E \rightarrow Z$ isomerizes with internal hydrogen (of the amine moiety) bridging to the ketone oxygen (camphor skeleton) rendering *trans*-$[MCl_2(MeHNNC_{10}H_{14}O)_2]$ (M = Pd or Pt) more stable and less basic thus agreeing with the observed catalytic behaviour.

The high sensitivity of the catalysts to the characteristics of Y prompted us to check if other parameters influence the process. A first tentative was replacement of chloride by bromide in *trans*-$[PdBr_2(YNC_{10}H_{14}O)_2]$ (Y = $NMe_2$ **2a**, $NH_2$ **2c**, OH **2d**, Ph **2g**).

Analysis by X-rays of a crystal of *trans*-$[PdBr_2(Me_2NNC_{10}H_{14}O)_2]$ shows that the complex has square planar geometry, the camphorimine ligands coordinate the metal through the imine nitrogen atom occupying mutually *trans* positions (Fig. 4) such as in *trans*-$[PdCl_2(Me_2NNC_{10}H_{14}O)_2]$ [17] or *trans*-$[PtCl_2(Me_2NNC_{10}H_{14}O)_2]$ [2]. From the X-ray structure (Fig. 4) it came out that bromide ligands do not introduce relevant structural differences compared to chloride in related complexes *trans*-$[PdX_2(Me_2NNC_{10}H_{14}O)_2]$. Thus, the halide must account for different catalytic properties if there are some.

For comparative purposes the catalytic properties of *trans*-$[PdBr_2(Me_2NNC_{10}H_{14}O)_2]$ were evaluated by following the formation of **B** and **C** as previously. In this case the experimental fittings did not converge (correlation factor 92%) pointing to other reactions being involved in the process. In fact, by including A → D and C → D processes in the equations the fitted and experimental data converged to 98% (Fig. 5) and the rate constants were calculated $k_1 = 2.0 \times 10^{-5}$ (% $A_0 \times min^{-1}$ and $k_2 = 1.4 \times 10^{-5}$ (% $A_0 \times min)^{-1}$). Kinetic constants are three orders of magnitude lower than those for the related chloride catalyst (Table 1). Bromide steric effects may account for small nucleophiles such as $H_2O$ becoming competitive enabling A → D conversion.




**Scheme 2.**

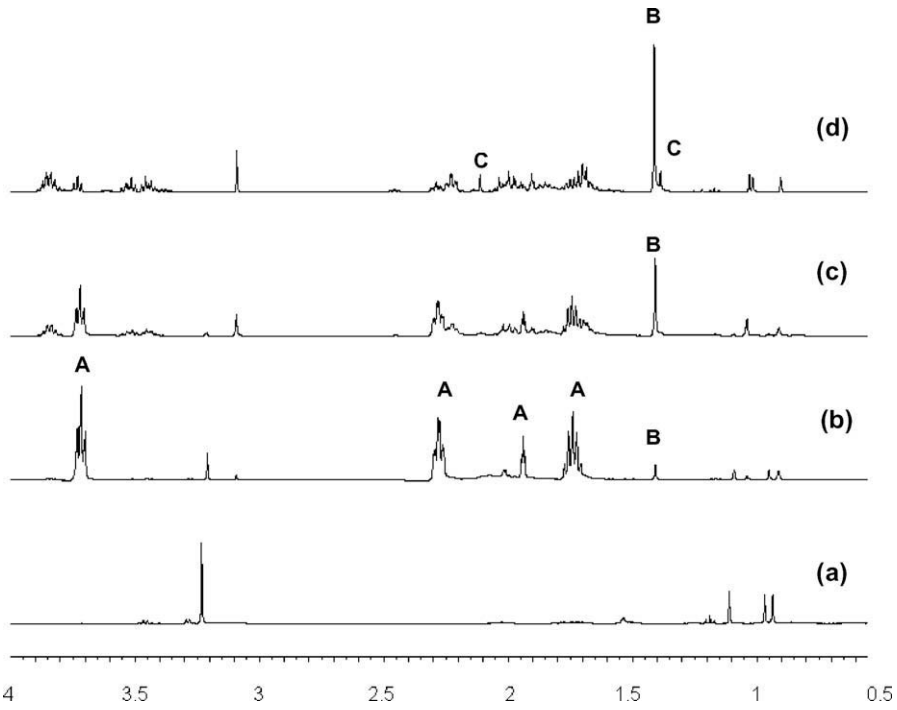



**Fig. 2.** $^1$H NMR spectra of: (a) *trans*-[$PdCl_2(Me_2NNC_{10}H_{14}O)_2$] in $CDCl_3$; (b) 4 min after addition of 4-pentyn-1-ol (**A**) to the catalyst solution; (c) the maximum amount of 2-methyl-2-pent-4-ynyloxy-tetrahydrofuran (**B**) is reached after 2 h; (d) product of hydration (**C**).

**Table 1**
Maximum yield of **B**[a] and kinetic constants for processes catalysed by *trans*-[$PdCl_2(YNC_{10}H_{14}O)_2$] complexes.

| | Y | **B** (% $A_0$) | $k_1$ (% $A_0 \times$ min)$^{-1}$ | $k_2$ (% $A_0 \times$ min)$^{-1}$ |
|---|---|---|---|---|
| **1c** | $NH_2$ | 41 | $2.57 \times 10^{-2}$ | $1.76 \times 10^{-3}$ |
| **1b** | NHMe | 29 | $5.95 \times 10^{-5}$ | $1.78 \times 10^{-5}$ |
| **1a** | $NMe_2$ | 33 | $1.54 \times 10^{-2}$ | $4.83 \times 10^{-3}$ |
| **1d** | OH | 42[b] | $2.03 \times 10^{-2}$ | $1.26 \times 10^{-3}$ |
| **1e** | OMe | 37[c] | $7.70 \times 10^{-5}$ | $3.14 \times 10^{-5}$ |
| **1f** | Pr[i] | 11[d] | $5.43 \times 10^{-7}$ | $5.63 \times 10^{-7}$ |
| **1g** | Ph | 2.5[d] | $5.64 \times 10^{-8}$ | $1.72 \times 10^{-7}$ |

[a] Calculated after 2 h reaction unless stated otherwise. Referred to initial 4-penty-1-nol ($A_0$) (due stoichiometry the expected maximum value is 50%, Scheme 2).
[b] 2.25 h.
[c] 2.5 h.
[d] 1.5 h.

Solubility problems precluded kinetic study of *trans*-[$PdBr_2(H_2NNC_{10}H_{14}O)_2$] and evaluation of the constants for reaction with 4-pentyn-1-ol.

To have an insight into the influence of the transition metal in the upper catalytic processes complexes *trans*-[$PtCl_2L_2$] (L = $YNC_{10}H_{14}O$; Y = $NMe_2$ **3a**, NHMe **3b**, $NH_2$ **3c**) were synthesised and their reaction with 4-pentyn-1-ol followed by NMR as before. The simulated and experimental data for A → B and B → C processes agree by a factor no lower than 98% such as in the case of Pd-Cl (Fig. 6) catalysts.

The rate constants for ($k_1$, $k_2$, Table 2) are roughly four orders of magnitude lower than those calculated for the corresponding palladium catalysts in agreement with palladium playing an essential role in the processes. The *Z* conformation of the camphor hydrazone ligand in *trans*-[$PtCl_2(MeHNNC_{10}H_{14}O)_2$] retards the catalytic process (Table 2) such as observed for the palladium complex (Table 1).

Calculated turnover numbers (TON, Fig. 7) and turnover frequencies (TOF, Fig. 8) state on the effectiveness of *trans*-[$MX_2(YNC_{10}H_{14}O)_2$] catalysts for synthesis of **B**. TON values do not differ much from Pd to Pt chloride systems (Fig. 7), although they are slightly lower in the case of Pd-bromide system. In spite of that, all complexes can be considered as efficient for promotion of A → B conversion: the apparent modesty of TON values is due to the experimental conditions, i.e. concentrations ratios (30 > **A**/cat > 25). The activities ($A_i$) of complexes *trans*-[$PdCl_2(YNC_{10}H_{14}O)_2$] (Y = $NH_2$: $A_i$ = 168 ton; NOH: $A_i$ = 150 ton and $NMe_2$: $A_i$ = 166 ton, Table 3) calculated as weight of **B** produced per mole of catalysts per mole of substrate (**A**) per hour, are very attractive under synthetic purposes and can still be enhanced by decreasing catalyst loading, as shown for complex **1a** ($A_i$ = 166 ton; *ca.* 2% catalyst and 241 ton; *ca.* 0.5% catalyst).

TOF values (calculated at the highest concentration of **B**) as expected follow the same trend as $k_1$, i.e. all palladium-chloride catalysts display higher TOF values than the platinum-chloride or palladium-bromide catalysts (Fig. 8) except *trans*-[$PdBr_2(HONC_{10}H_{14}O)_2$] that displays a TOF value in the same range (TOF ≈ 10) of *trans*-[$PdCl_2(YNC_{10}H_{14}O)_2$] pointing to the relevance of the camphorimine Y group in the process. In this case the basic/protic characteristics of Y (OH) overcome the retarding effect of the halide (Br).

In this study we aimed to get insight into the process that converts A → B and B → C thus the experimental conditions that enhance TON, TOF for formation of **B** were not optimized. Under synthetic applications a strict control of the purity of 4-pentyn-1-ol and water in the solvent as well as the reaction time (no longer than 2 h) will be necessary to inhibit formation of **C** and improve yields in **B**.

## 3. Conclusions

Irrespectively of the metal (Pd or Pt) or the halide (Cl or Br) the camphor complexes *trans*-[$MX_2L_2$] (M = Pd or Pt; X = Cl or Br; L = $YNC_{10}H_{14}O$) catalyze conversion of 4-pentyn-1ol into 2-methyl-2-pent-4-ynyloxy-tetrahydrofuran with efficiencies highly dependent of Y.

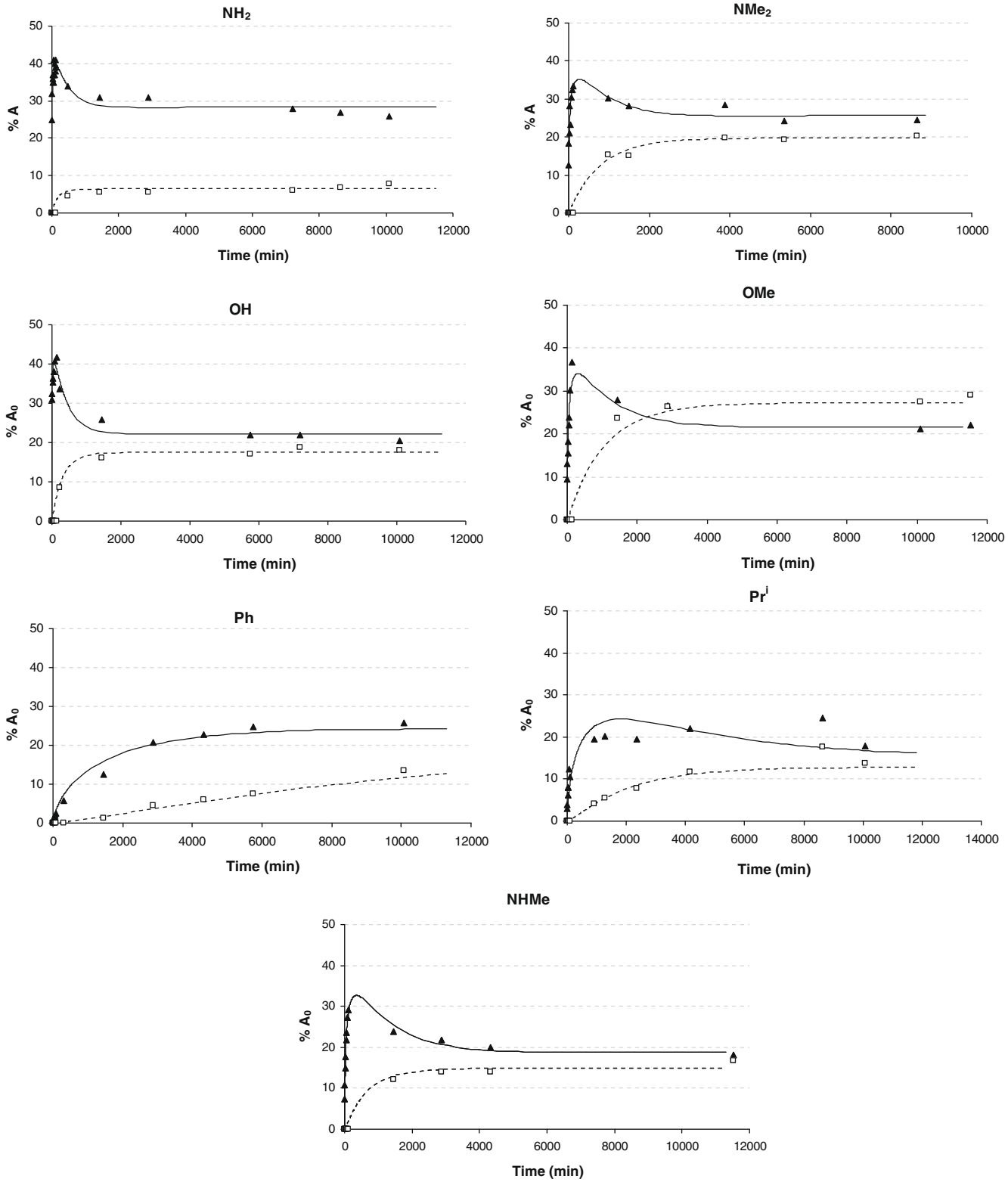



**Fig. 3.** **B** (experimental ▲, fit —) or **C** (experimental □, fit ---) measured vs. initial 4-pentyn-1-ol (% $A_0$) in processes catalysed by complexes *trans*-$[PdCl_2L_2]$ (L = $YNC_{10}H_{14}O$).

High basic ($NMe_2$) and/or protic (OH, $NH_2$) Y groups at the camphorimine ligand ($YNC_{10}H_{14}O$) enable the formation of 2-methyl-2-pent-4-ynyloxy-tetrahydrofuran. Stabilization by the camphor ligand (through Y) of the alcohol group in the activated 4-pentyn-1-ol conceivably inhibits ready cyclization enabling formation of 2-methyl-2-pent-4-ynyloxy-tetrahydrofuran within a reactivity pattern not observed with other catalysts.

The best catalyst from those under study is *trans*-$[PdCl_2(H_2NNC_{10}H_{14}O)_2]$ in close resemblance with *trans*-$[PdCl_2(YNC_{10}H_{14}O)_2]$ ($NMe_2$ or OH).

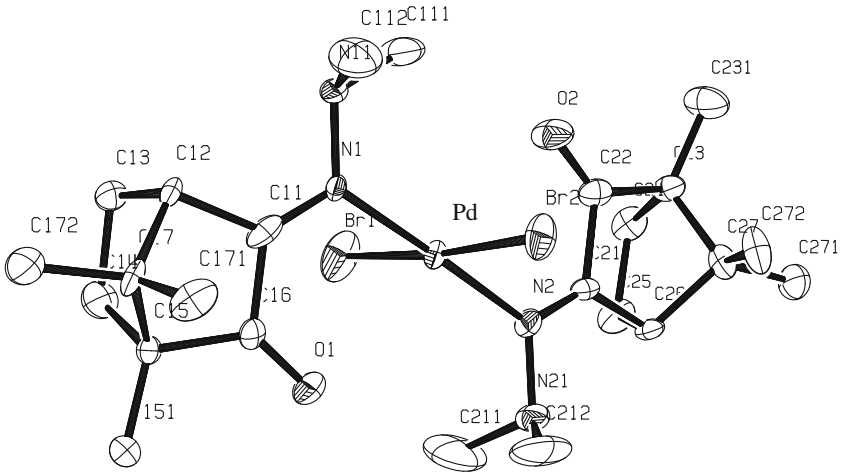



**Fig. 4.** ORTEP drawing for *trans*-[$PdBr_2(Me_2NNC_{10}H_{14}O)_2$] showing atom labeling scheme. Pd–N(av) = 2.04 Å; Pd-Br(av) = 2.45 Å; N–C(av) = 1.30 Å; N–N(av) = 1.43 Å; N–$CH_3$(av) = 1.50 Å; C–O(av) = 1.19 Å. Br–Pd–Br = 174.5°; N–Pd–N = 177.2°; N–Pd–Br(av) = 90.0°.

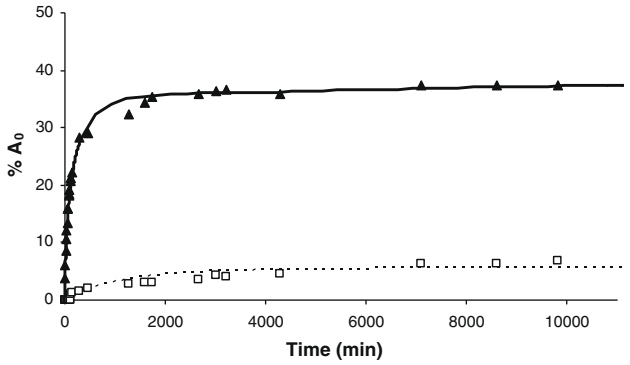



**Fig. 5. B** (experimental ▲, fit —) or **C** (experimental □, fit - - -) measured vs. initial 4-pentyn-1-ol (% $A_0$) catalysed by *trans*-[$PdBr_2$ ($Me_2NNC_{10}H_{14}O)_2$].

## 4. Experimental section

All the experiments were carried out under inert atmosphere. The solvents (Fluka or Panreac) were purified by conventional techniques and distilled under dinitrogen immediately before use. Palladium chloride, palladium benzonitrile dichloride, palladium bromide, platinum chloride and 4-pentyn-1-ol were purchased from Aldrich. Complexes [$MCl_2(YNC_{10}H_{14}O)_2$] (M = Pd: Y = $NMe_2$, NHMe, OH, $Pr^i$, Ph and Pt: Y = $NMe_2$, NHMe were prepared by published methods [1,2,17].

NMR spectra ($^1$H, $^{13}$C, DEPT, HSQC HMBC) were obtained in $CDCl_3$ using a Bruker 400 MHz Avance II$^+$ Spectrometers. Chemical shifts are referred to TMS ($\delta$ = 0 ppm). IR spectra were obtained in a JASCO FTIR 430 spectrometer.

The catalytic experiments were conducted in a sure seal NMR tube using degassed $CDCl_3$ (CIL). Typically $CDCl_3$ (*ca.* 0.3 mL) was added to the catalyst precursor (ML, 0.0050 g) and the $^1$H NMR spectrum obtained. Then, 50 μL of 4-pentyn-1-ol were introduced into the tube through the septa and the reaction followed by $^1$H NMR. Due to limitations of the equipment the first spectra could not be obtained before 3–4 min after addition of the alkynol. From time to time $^{13}$C NMR was obtained to corroborate the presence of A B, C and D.

### 4.1. X-ray diffraction analysis

X-ray diffraction analysis was performed on a orange crystal of *trans*-[$PdBr_2(Me_2NNC_{10}H_{14}O)_2$] (0.4 × 0.3 × 0.3 mm) obtained from a $CH_2Cl_2$ solution. Data was collected on a Bruker AXS-KAPPA APEX II area detector apparatus using graphite-monochromated Mo Kα (λ = 0.71073 Å) and were corrected for Lorentz, polarization and empirically for absorption effects. Cell dimensions were determined from the setting angles of 8889 reflections. Complex crystallizes in the tetragonal space group $P4_3$. The structure was solved by direct methods using SHELX97 [18] and refined by fullmatrix least-squares against $F^2$ using SHELX97 all included in the suit of programs WinGX v1.70.01 for Windows [19].

Non-hydrogen atoms were refined anisotropically and H atoms were inserted in idealized positions and allowed to refine riding on the parent carbon atom. Crystal data and refinement parameters are summarized in Table 4. Illustrations of the molecular structures were made with ORTEP3 [20].

### 4.2. Digital simulation

The experimental data was obtained by integration of the signals of **B** and **C** in the $^1$H NMR spectra. The signals of the methyl groups at the camphor skeleton in [$MX_2(YNC_{10}H_{14}O)_2$] were used as internal reference throughout each experiment.

A FORTRAN subroutine was written to perform the numerical integration of the complete set of equations (using steps of 0.01 min) considering the generic mechanism below:

$$\text{(i)}\ [MX_2L_2] + A \overset{K}{\rightleftarrows} [MX_2L(A)] + L$$

$$\text{(ii)}\ [MX_2L(A)] + A \overset{k}{\rightarrow} [MX_2L(B)]$$

$$\text{(iia)}\ [MX_2L(B)] + L \overset{fast}{\rightarrow} [MX_2L_2] + B$$

The output was then fed to a least-squares routine and the generated values optimized till agreement with experimental data was no lower than 98%. The graphical plots were made using Excel Worksheets.

### 4.3. Synthesis

#### 4.3.1. Organic species

Camphorimine compounds ($YNC_{10}H_{14}O$) used as ligands were prepared from (+)-camphorquinone by published methods (Y = $NMe_2$, OMe, OH, *iso*-Pr [21–23]) or by improving ancient techniques [24], typically as described.

(1*R*,4*S*)-3-(2,2-Diphenylhydrazono)-1,7,7-trimethylbicyclo[2.2.1] heptan-2-one (Y = $NPh_2$) - Diphenylhydrazine hydrochloride (1.35 g, 7.3 mmol), 7,7-trimethylbicyclo-[2.2.1]heptane-2,3-dione

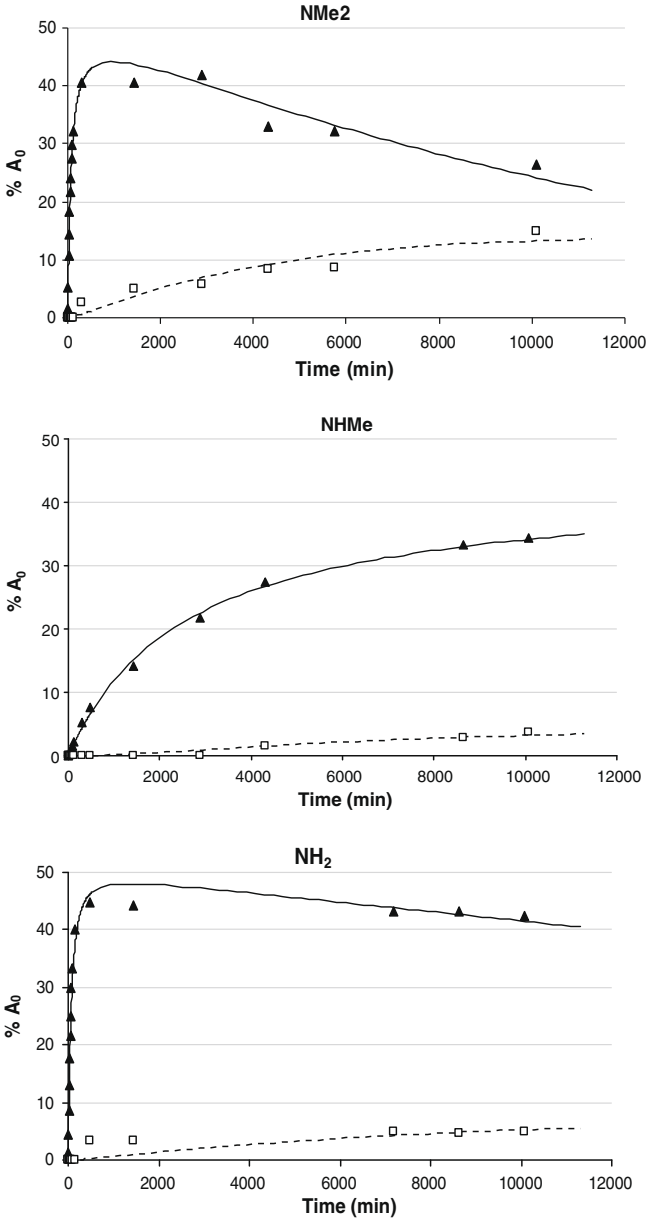



**Fig. 6.** **B** (experimental ▲, fit —) or **C** (experimental □, fit - - -) measured vs. initial 4-pentyn-1-ol (% $A_i$) in processes catalysed by complexes *trans*-[$PtCl_2(YNC_{10}H_{14}O)_2$].

**Table 2**
Calculated constants for A → B and B → C conversion promoted by *trans*-[$PtCl_2(YNC_{10}H_{14}O)_2$] (**3**).

| | Y | $k_1$ (% $A_0 \times$ min)$^{-1}$ | $k_2$ (% $A_0 \times$ min)$^{-1}$ |
|---|---|---|---|
| **3a** | $NMe_2$ | $2.43 \times 10^{-6}$ | $1.39 \times 10^{-8}$ |
| **3b** | NHMe | $3.94 \times 10^{-8}$ | $1.61 \times 10^{-7}$ |
| **3c** | $NH_2$ | $2.11 \times 10^{-6}$ | $1.41 \times 10^{-9}$ |

((1R)-camphorquinone) (1.02 g, 6.1 mmol) and sodium acetate were stirred in glacial acetic acid (12 mL) at room temperature for 2 days. By addition of distilled water (60 mL) to the solution a yellow precipitate formed that upon filtration and drying afforded the title compound (1.95 g, 5.9 mmol), Yield 96%. Elemental Anal. Calc. for $C_{22}H_{24}O \cdot 5/4CH_2Cl_2$: C, 74.4; N, 7.9; H, 7.5. Found: C, 74.2; N, 8.0; H, 6.9%. IR ($cm^{-1}$) 1728 ($\nu_{CO}$), 1572 ($\nu_{CN}$), 1587 ($\nu_{Ph}$). $^1H$ NMR ($CDCl_3$, $\delta$ ppm): 7.40–7.15 (m, 10H), 1.42 (d,

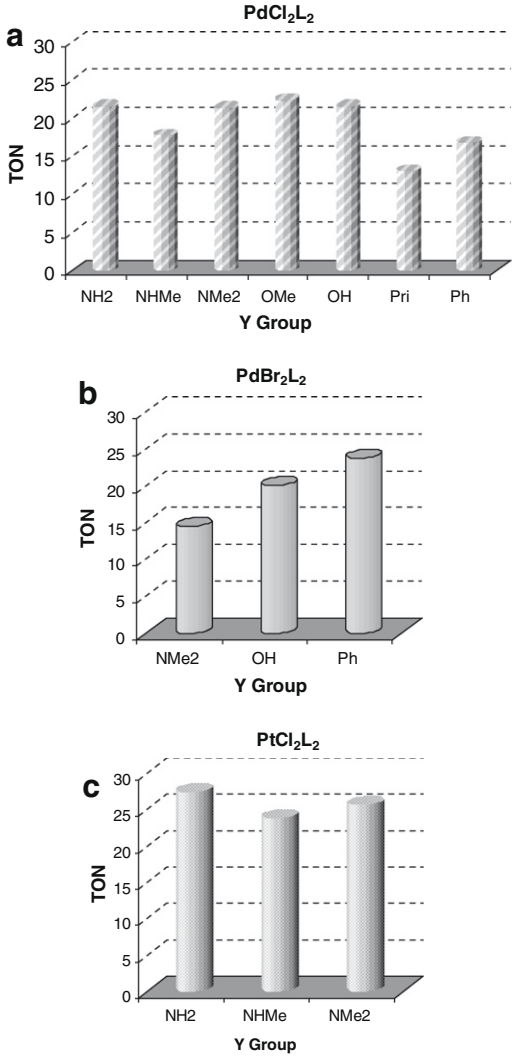



**Fig. 7.** Turnover numbers for: (a) *trans*-[$PdCl_2(YNC_{10}H_{14}O)_2$]; (b) *trans*-[$PdBr_2(YNC_{10}H_{14}O)_2$] and (c) *trans*-[$PtCl_2(YNC_{10}H_{14}O)_2$].

$J_{HH}$ = 4.0, 1H), 1.70–1.22 (m, 4H), 0.96 (s, 3H), 0.74 (s, 3H), 0.69 (s, 3H). $^{13}C$ NMR ($CDCl_3$, $\delta$ ppm): 205.8 (CO), 146.8 (CN), 145.4 (*ipso*-Ph), 122.8 (*m*-Ph), 125.5 (*p*-Ph), 129.5 (*o*-Ph), 56.8 (C1), 49.6 (C4), 45.2 (C7), 30.6 (C6), 24.1 (C5), 20.6, 17.8 (C9,10), 9.2 (C8).

(1*R*,4S)-3-(1,7,7-Trimethyl · bicyclo[2.2.1]heptane-2,3-dione3-(O-methyl-oxime) (Y = OMe) – a suspension of (1R)-camphorquinone monoxime (Y = OH) (0.165 g, 0.99 mmol) and sodium hydride (60%, dispersion in mineral oil) (0.037 g, 0.92 mmol) were stirred in THF (5 mL) for 45 min. Then, dimethyl sulfate (0.1 mL, 1.1 mmol) was slowly added and the mixture stirred for more 1 h. The mixture was taken close to dryness and $H_2O$ (2 mL) added. The organic layer was then extracted with $CH_2Cl_2$ (2 × 20 mL) and dried over $MgSO_4$. By filtration and slow evaporation of the solvent the camphor compound precipitate as a yellow solid (0.13 g, 0.67 mmol), Yield 67%. IR ($cm^{-1}$) 1743 ($\nu_{CO}$), 1634 ($\nu_{CN}$). $^1H$ NMR ($CDCl_3$, $\delta$ ppm): 4.00 (s, 3H), 3.11 (d, $J_{HH}$ = 4.4, 1H), 1.16–2.07 (m, 4H), 1.00 (s, 3H), 0.85 (s, 3H), 0.96 (s, 3H). $^{13}C$ NMR ($CDCl_3$, $\delta$ ppm): 204.1 (CO), 158.8 (CN), 63.0 ($OCH_3$), 58.4 (C1), 47.1 (C4), 44.8 (C7), 30.7 (C6), 23.9 (C5), 20.7, 17.6 (C9,C10), 9.0 (C8).

### 4.3.2. Complexes

*trans*-[$PdCl_2(H_2NNC_{10}H_{14}O)_2$] – $PdCl_2$ (0.15 g, 0.86 mmol) plus 3-$H_2NNC_{10}H_{14}O$ (0.398 g, 2.21 mmol) were stirred in dichloro-

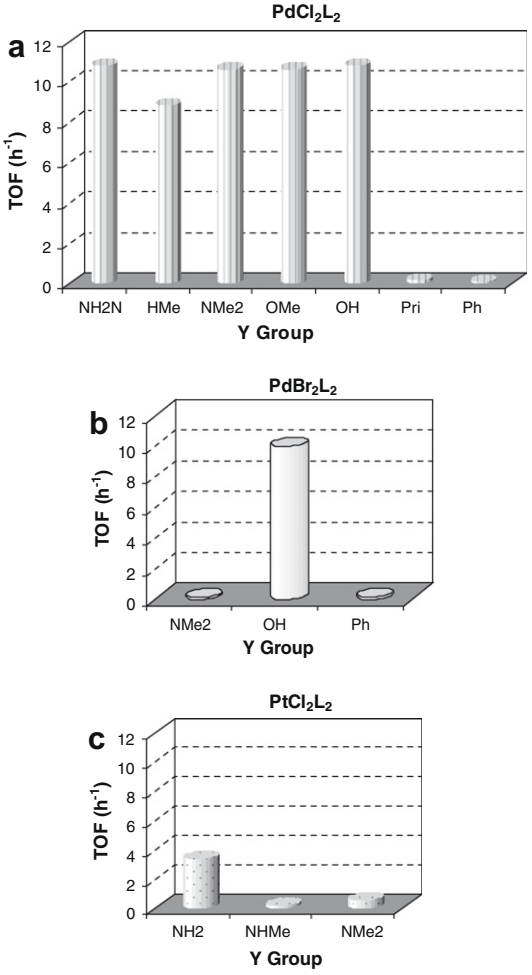



**Fig. 8.** TOF values calculated for (a) *trans*-[$PdCl_2(YNC_{10}H_{14}O)_2$]; (b) *trans*-[$PdBr_2(YNC_{10}H_{14}O)_2$] and (c) *trans*-[$PtCl_2(YNC_{10}H_{14}O)_2$].

**Table 3**
Calculated activities[a].

| Y | Activity ton of **B** per (mol cat × mol A × hr) | | |
|---|---|---|---|
| | X = Cl | | X = Br |
| | Pd | Pt | Pd |
| $NH_2$ | 168 | 8.57 | – |
| NHMe | 139 | 1.94 | – |
| $NMe_2$ | 166 | 8.35 | 2.31 |
| OH | 150 | – | 157 |
| OMe | 140 | – | – |
| $Pr^i$ | 1.41 | – | – |
| Ph | 1.55 | – | 2.59 |

[a] A → B conversion promoted by *trans*-[$MX_2(YNC_{10}H_{14}O)_2$] catalysts.

methane (50 mL) for 13 days after which the brown suspension was filtered to remove unreacted $PdCl_2$ (0.050 g, 0.28 mmol). The solution was taken to dryness and the solid dissolved in $Et_2O$ (15 mL). Filtration to remove traces of 3-$H_2NNC_{10}H_{14}O$ followed by solvent evaporation to *ca.* 3 mL and by addition of *n*-hexane (8 mL) afforded the complex as a reddish solid (0.14 g, 0.26). Yield 30%. Elemental Anal. Calc. for $PdCl_2C_{20}H_{32}N_4O_2 \cdot \frac{1}{3}n$-hexane: C, 46.7; N, 9.9; H, 6.5. Found: C, 46.4; N, 9.6; H, 6.6%. IR ($cm^{-1}$) 3365, 3241 ($\nu_{NH2}$), 1716 ($\nu_{CO}$), 1577 ($\nu_{CN}$). $^1H$ NMR ($CDCl_3$, $\delta$ ppm): 7.72 (s, 4H), 3.76 (d, $J_{HH}$ = 3.9, 2H), 2.21–1.18 (m, 8H), 1.03 (s, 6H), 0.97 (s, 6H), 0.91 (s, 6H). $^{13}C$ NMR ($CDCl_3$, $\delta$ ppm): 201.3 (CO), 156.1 (CN), 59.9 (C1), 54.3 (C4), 47.2 (C7), 30.2 (C6), 24.7 (C5), 21.1, 17.9 (9,10), 8.8 (C8).

**Table 4**
Crystal data and structure refinement for *trans*-[$PdBr_2(C_{12}H_{20}N_2O)_2$].

| | |
|---|---|
| Empirical formula | $C_{24}H_{40}Br_2N_4O_2Pd$ |
| Formula weight | 682.74 |
| Temperature (K) | 293(2) |
| Wavelength (Å) | 0.71073 |
| Crystal system, space group | $P4_3$ |
| *Unit cell dimensions* | |
| *a* (Å) | 10.0280(7) |
| *b* (Å) | 10.0280(7) |
| *c* (Å) | 27.635(4) |
| $\alpha$ (°) | 90 |
| $\beta$ (°) | 90 |
| $\gamma$ (°) | 90 |
| Volume ($A^3$) | 2779.0(5) |
| *Z* | 4 |
| Calculated density ($Mg/m^3$) | 1.608 |
| Absorption coefficient ($mm^{-1}$) | 3.569 |
| *F*(000) | 1336 |
| Crystal size (mm) | 0.2 × 0.1 × 0.08 |
| $\theta$ Range for data collection | 0.74–31.92 |
| Limiting indices | $-14 \leqslant h \leqslant 14$, $-5 \leqslant k \leqslant 10$, $-39 \leqslant l \leqslant 40$ |
| Reflections collected/unique | 17167/8889 [$R_{(int)}$ = 0.0550] |
| Completeness to $\theta$ = 31.92 | 97.1% |
| Absorption correction | None |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data/restraints/parameters | 8889/0/298 |
| Goodness-of-fit on $F^2$ | 0.851 |
| Final *R* indices [$I > 2\sigma(I)$] | $R_1$ = 0.0398, $wR_2$ = 0.0782 |
| R indices (all data) | $R_1$ = 0.0671, $wR_2$ = 0.1048 |
| Absolute structure parameter | 0.013(14) |
| Largest diff. peak and hole (e $A^{-3}$) | 0.613 and −0.721 |

*trans*-[$PdCl_2(HONC_{10}H_{14}O)_2$] – [$PdCl_2(NCC_6H_5)_2$] (0.20 g, 0.52 mmol) and 3-$HONC_{10}H_{14}O$ (0.19 g, 1.04 mmol) were mixed and stirred in dichloromethane (40 mL) for 1 h. The solvent was evaporated (to *ca.* 2 mL) and by addition of $Et_2O$ (5 mL) followed by n-hexane (1 mL) the complex precipitate as a yellow solid (0.080 g, 0.15 mmol), Yield 29%. IR ($cm^{-1}$) 3445 ($\nu_{OH}$), 1755 ($\nu_{CO}$), 1657 ($\nu_{CN}$). $^1H$ NMR ($CDCl_3$, $\delta$ ppm): 10.67 (s, 2H), 3.26 (d, $J_{HH}$ = 2.2, 2H), 2.10–1.48 (m, 8H), 1.11 (s, 6H), 0.98 (s, 6H), 0.91 (s, 6H). $^{13}C$ NMR ($CDCl_3$, $\delta$ ppm): 199.8 (CO), 165.4 (CN), 59.2 (C1), 53.4 (C4), 45.3 (C7), 30.1 (C6), 23.6 (C5), 21.1, 17.6 (C9,10), 9.1 (C8).

*trans*-[$PdBr_2(Me_2NNC_{10}H_{14}O)_2$] – $PdBr_2$ (0.11 g, 0.41 mmol) and 3-$Me_2NNC_{10}H_{14}O$ (0.17 g, 0.82 mmol) were stirred for two days in $CH_2Cl_2$ (40 mL). Traces of unreacted $PdBr_2$ (0.010 g) were filtered and the volume of the solution reduced under vacuum to *ca.* 10 mL. Upon addition of $Et_2O$ (8 mL) the solution was allowed to stand overnight in the fridge. Bright orange crystals were obtained that were filtered and dried under vacuum (0.12 g, 0.18 mmol), Yield 43%. Elemental Anal. Calc. for $PdBr_2C_{24}H_{40}N_4O_2$: C, 42.2; N, 8.2; H, 5.9. Found: C, 41.9; N, 8.0; H, 6.1%. IR ($cm^{-1}$), 1757 ($\nu_{CO}$), 1608 ($\nu_{CN}$). $^1H$ NMR ($CDCl_3$, $\delta$ ppm): 3.27 (d, $J_{HH}$ = 3.3, 2H), 3.24 (s, 6), 2.12–1.52 (m, 8H), 1.10 (s, 6H), 0.96 (s, 6H), 0.93 (s, 6H). $^{13}C$ NMR ($CDCl_3$, $\delta$ ppm): 201.7 (CO), 174.5 (CN), 58.5 (C1), 54.9 (C4), 49.6 ($N(CH_3)_2$), 44.9 (C7), 30.1 (C6), 24.1 (C5), 21.2, 17.9 (C9,10), 9.4 (C8).

*trans*-[$PdBr_2(H_2NNC_{10}H_{14}O)_2$] ¼ $CH_2Cl_2$ – $PdBr_2$ (0.208 g, 0.78 mmol) and 3-$H_2NNC_{10}H_{14}O$ (0.321 g, 1.78 mmol) were stirred in dichloromethane (25 mL) for 3 days. The complex precipitated as a yellow solid that was filtered off and dried (0.40 g; 0.64 mmol), Yield, 82%. Elemental Anal. Calc. for $PdBr_2C_{20}H_{32}N_4O_2$: C, 36.3; N, 8.4; H, 4.9. Found: C, 36.5; N, 8.7; H, 5.0%. IR ($cm^{-1}$): 3258, 3176 ($\nu_{NH2}$), 1743 ($\nu_{CO}$), 1607 ($\nu_{CN}$). $^1H$ NMR (DMSO, $\delta$ ppm): 8.5–8.1 (br), 2.97 (d; $J_{HH}$ = 2.0, 2H), 1.97–1.19 (m, 8H), 0.87 (s, 3H), 0.81 (s, 3H) 0.68 (s, 3H). $^{13}C$ NMR ($CDCl_3$, $\delta$ ppm): 203.6 (CO), 145.9 (CN), 57.3 (C1), 45.0 (C7), 44.5 (C4), 31.0 (C6), 23.5 (C5), 20.2, 18.0 (C9,10), 9.2 (C8).

*trans*-[$PdBr_2(HONC_{10}H_{14}O)_2$] – $PdBr_2$ (0.259 g, 0.97 mmol) and 3-$HONC_{10}H_{14}O$ (0.406 g, 2.24 mmol) were stirred in dichloromethane (40 mL) for 3 days. The suspension was filtrated to remove traces of $PdBr_2$. By solvent evaporation an orange solid precipitates that upon filtration and washing with $Et_2O$ (5 mL) affords the title complex (0.12 g, 0.19 mmol), Yield 20%. Elemental Anal. Calc. for $PdBr_2C_{20}H_{30}N_2O_4$: C, 35.4; N, 3.9; H, 4.5. Found: C, 35.2; N, 4.0; H, 4.5%. IR ($cm^{-1}$): 3535 ($\nu_{OH}$), 1755 ($\nu_{CO}$), 1616 ($\nu_{CN}$). $^1H$ NMR ($CDCl_3$, $\delta$ ppm): 3.33 (d, $J_{HH}$ = 4.0, 2H), 3.07 (s, 2H), 2.02–1.15 (m, 8H), 1.07 (s, 6H), 0.98 (s, 6H), 0.92 (s, 6H). $^{13}C$ NMR ($CDCl_3$, $\delta$ ppm): 202.0 (CO), 165.3 (CN) 59.4 (C1), 53.4 (C4), 45.4 (C7), 30.1 (C6), 23.7 (C5), 21.1, 17.6 (C9,10), 9.0 (C8).

*trans*-[$PdBr_2(PhNC_{10}H_{14}O)_2$] – $PdBr_2$ (0.26 g, 0.97 mmol) and 3-$PhNC_{10}H_{14}O$ (0.54 g, 2.2 mmol) were stirred in dichloromethane (30 mL) for 3 days. The suspension was filtrated to remove traces of $PdBr_2$. Solvent evaporation to *ca.* 2 mL followed by addition of $Et_2O$ (4 mL) allowed an orange solid to precipitate that upon filtration afforded the title complex (0.25 g, 0.19 mmol), Yield 30%. Elemental Anal. Calc. for $PdBr_2C_{32}H_{38}N_2O_2$: C, 50.4; N, 3.6; H 5.0. Found: C, 50.5; N, 3.7; H, 5.2. IR ($cm^{-1}$): 1661 ($\nu_{CO}$), 1591 ($\nu_{CN}$). $^1H$ NMR ($CDCl_3$, $\delta$ ppm): 7.57−7.36 (m, 10H), 2.67 (d, $J_{HH}$ = 4.8, 2H), 1.95−1.49 (m, 8H), 1.06 (s, 6H), 0.93 (s, 6H), 0.86 (s, 6H). $^{13}C$ NMR ($CDCl_3$, $\delta$ ppm): 199.8 (CO), 181.1 (CN), 147.1 (*ipso*-Ph), 129.1 (*m*-Ph), 127.8 (*p*-Ph), 123.3 (*o*-Ph), 58.6 (C1), 53.6 (C4), 45.0 (C7), 29.4, 24.2 (C9,10), 21.4, 17.5 (C9,10), 9.2 (C8).

*trans*-[$PtCl_2(H_2NNC_{10}H_{14}O)_2$] – dichloromethane (70 mL) was added to $PtCl_2$ (0.15 g, 0.56 mmol) and 3-$H_2NNC_{10}H_{14}O$ (0.250 g, 1.39 mmol) and the mixture stirred for 8 days. The brown suspension was then filtered to remove unreacted $PtCl_2$ (0.050 g, 0.19 mmol) and the solvent reduced to *ca.* 5 mL. By addition of $Et_2O$ (15 mL) traces of a minor complex isomer precipitated and were removed by filtration. Upon complete evaporation of the solvent and washing with *n*-hexane the complex was obtained as a light red solid (0.076 g, 0.12 mmol), Yield 33%. Elemental Anal. Calc. for $PtCl_2C_{20}H_{32}N_4O_2$: C, 36.1; N, 8.1; H, 4.9. Found: C, 36.4; N, 7.9; H, 4.9%. IR ($cm^{-1}$): 3377, 3246 ($\nu_{NH2}$), 1716 ($\nu_{CO}$), 1578 ($\nu_{CN}$). $^1H$ NMR ($CDCl_3$, $\delta$ ppm): 3.79 (d, $J_{HH}$ = 4.3, 2H), 3.07 (s, 2H), 2.24–1.23 (m, 8H), 1.02 (s, 6H), 0.98 (s, 6H), 0.92 (s, 6H). $^{13}C$ NMR ($CDCl_3$, $\delta$ ppm): 202.2 (CO), 156.6 (CN), 59.7 (C1), 53.9 (C4), 46.8 (C7), 30.2 (C6), 24.5 (C5), 21.3, 17.8 (C9,10), 8.9 (C8).

## 5. Supplementary material

CCDC 697433 contains 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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