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Catalytic activity of palladium(II) complexes with tridentate nitrogen ligands in the hydrogenation of alkenes and alkynes

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Abstract

A series of palladium(II) complexes with the nitrogen ligands *N*-pyridin-2-yl-*N*′-pyridin-2-ylmethylene-hydrazine (**HL^1**), and *N*,*N*-dimethyl-*N*′-pyridin-2-ylmethylene-ethane-1,2-diamine, (**L^2**) have been synthesised and their catalytic activity in the hydrogenation of alkenes and alkynes in mild conditions ($P_{H_2} = 1$ atm, $T = 40\,^{\circ}C$) has been studied. Ligand **L^2** behaves as tridentate in the complexes Pd(**L^2**)Cl_2 (**4**) and [Pd(**L^2**)Cl](OTf) (**5**), whose catalytic activity is negligible in the hydrogenation of the tested substrates (styrene and phenylacetylene). The complexes Pd(**L^1**)Cl (**1**) and Pd(**L^1**)(OAc) (**2**) show a good catalytic activity towards styrene and phenylacetylene under homogeneous conditions. The high insolubility of the complex Pd_3(**L^1**)$_2Cl_4$ (**3**) prevents its use as catalyst in homogeneous hydrogenations; however, it has been employed in heterogeneous conditions, showing a very good chemo- and stereo-selectivity in the semi-hydrogenation of alkynes (phenylacetylene, diphenylacetylene and 4-octyne).

Keywords: Palladium; Hydrogenation; Nitrogen ligands; Chemo-selectivity

1. Introduction

There is a considerable interest towards the semi-hydrogenation of alkynes catalysed by metals containing systems, both for academic and industrial purposes [1–3]. The major part of the examples reported in the literature concerns with hydrogenations carried out in heterogeneous conditions [4,5], and only few articles deal with homogeneous semi-hydrogenations catalysed by metal complexes [6,7]. Our group has recently demonstrated that the homogeneous chemo-selective hydrogenation of acetylenic substrates can be accomplished by palladium(II) complexes containing terdentate ligands of the type Pd(PNO)X [8] or Pd(NNS)X (X = OAc, Cl) [9]. In both cases, the ligands contain one soft atom (P or S) which is believed necessary in order to prevent palladium releasing during the reaction progress. With the aim of testing a different donor atoms set not containing soft atoms, we have focused our attention towards the trinitrogen ligands *N*-pyridin-2-yl-*N*′-pyridin-2-ylmethylene-hydrazine (**HL^1**) and *N*,*N*-dimethyl-*N*′-pyridin-2-ylmethylene-ethane-1,2-diamine (**L^2**) (Scheme 1). Different palladium(II) complexes containing these ligands have been prepared and used as catalysts in the homogeneous hydrogenation of styrene, phenylacetylene, 1,2-diphenylacetylene and 4-octyne. The extremely

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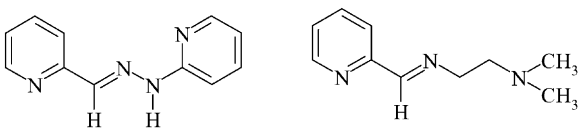


HL¹ **L²**

Scheme 1.

insoluble chloride complex **3** of stoichiometry $Pd_3(\mathbf{L^1})_2Cl_4$ has been used as catalysts in heterogeneous conditions.

2. Experimental

2.1. Synthesis

All the reactions were carried out under nitrogen, by using standard Schlenk techniques; the solvents were dried according to literature methods. All reagents of commercial quality were used without further purification.

Proton NMR spectra were recorded at 25 °C on a Bruker 300 FT spectrometer by using $SiMe_4$ as internal standard, while IR spectra were obtained with a Nicolet 5PCFT-IR spectrophotometer in the 4000–400 cm^{-1} range, using KBr disks. Elemental analyses were performed by using a Carlo Erba Model EA 1108 apparatus. MS-CI spectra were obtained by mean of a Finnigan SSQ710 spectrometer, collecting negative ions.

The preparations of ligand $\mathbf{L^2}$ [10], $\mathbf{HL^1}$ and its complexes [11] were made according to literature methods.

2.1.1. [Pd(L²)Cl]Cl (4)

An amount of 0.400 g (1.5 mmol) of $Pd(COD)Cl_2$ dissolved in 20 ml of dichloromethane were added to a dichloromethane solution (20 ml) of $\mathbf{L^2}$ (0.3 g, 1.6 mmol). After few minutes, a yellow precipitate was observed, which was filtered and washed with diethyl ether. ^{1}H NMR ($(CD_3)_2SO$): δ 8.77 (s, 1H, CH=N); 8.64 (d, 1H, H_1); 8.39 (t, 1H, H_3); 8.17 (d, 1H, H_4); 7.90 (t, 1H, H_2); 4.25 (t, 2H, H_6); 3.25 (t, 2H, H_5); 2.84 (sbr, 6H, CH_3). Anal. calc. for $C_{10}H_{15}Cl_2N_3Pd$ (354.5): C 33.87, H 4.26, N 11.85; found: C 33.98, H 4.09, N 11.07. MS (CI): *m/z* 318 [(M-Cl)$^-$].

2.1.2. [Pd(L²)Cl](OTf) (5)

An amount of 0.100 g (0.3 mmol) of **4** were dissolved in 20 ml of acetonitrile and an equimolar amount of silver triflate was added at room temperature. Immediately, silver chloride precipitated, which was filtered off and washed with acetonitrile. After concentration of the solution, a pale yellow powder was obtained, which was filtered, washed with diethyl ether and then dried in vacuum. ^{1}H NMR ($(CD_3)_2SO$): δ 8.77 (s, 1H, CH=N); 8.64 (d, 1H, H_1); 8.39 (t, 1H, H_3); 8.17 (d, 1H, H_4); 7.90 (t, 1H, H_2); 4.25 (t, 2H, H_6); 3.25 (t, 2H, H_5); 2.84 (sbr, 6H, CH_3). Anal. calc. for $C_{11}H_{15}ClF_3O_3SN_3Pd$ (468.2): C 28.21, H 3.22, N 9.01; found: C 27.99, H 3.31, N 9.12. MS (CI): *m/z* 318 [(M-OTf)$^-$].

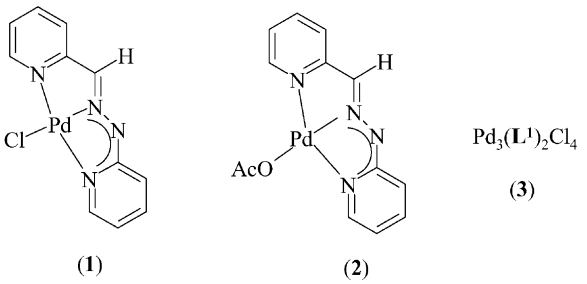
2.2. Catalysis

All the manipulations were carried out under nitrogen by using standard Schlenk techniques. The solvent (THF or *n*-hexane) was dried and stored under nitrogen. The GC analyses were performed on a Dani HP 3800 flame-ionisation gas chromatograph (OV 101 on CHP column). Styrene, phenylacetylene and 4-octyne were distilled in vacuum and stored under nitrogen. 0.04 mmol of complex were dissolved in 20 ml of dry solvent and the substrate was added in a 1:100 Pd/substrate molar ratio. The hydrogenation apparatus was analogous to that previously reported [8,9]. The progress of the reaction was monitored by gas chromatography. At the end of the reaction, the solution was conventionally worked up. The residue was analysed by IR spectroscopy, in order to confirm the unchanged nature of the catalyst. The stereo-chemistry of the products was established by analysing pure samples of the products.

3. Results and discussion

3.1. Synthesis

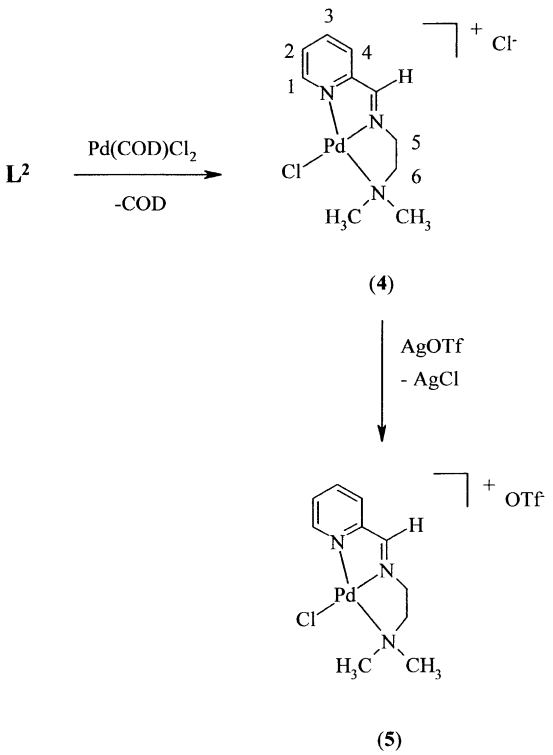
Scheme 1 shows ligands $\mathbf{HL^1}$ and $\mathbf{L^2}$; the mononuclear complexes Pd($\mathbf{L^1}$)Cl (**1**) and Pd($\mathbf{L^1}$)(OAc) (**2**), and the trinuclear complex $Pd_3(\mathbf{L^1})_2Cl_4$ (**3**) are shown in Scheme 2, while complexes [Pd($\mathbf{L^2}$)Cl]Cl (**4**) and [Pd($\mathbf{L^2}$)Cl](TfO) (**5**) are depicted in Scheme 3.



Scheme 2.

L^2 reacts with $Pd(COD)Cl_2$ in dichloromethane at room temperature giving rise to complex **4**. The reaction occurs with the fast displacement of the labile di-olefin ligand COD and the exclusion of a chloride anion from the co-ordination sphere, thus, the nitrogen ligand behaves as terdentate through the pyridine, the imine and the amine nitrogen atoms, and the square planar co-ordination of the metal is completed by a chloride ion. The solubility of the complex in polar solvents such as water, methanol and acetone is in accord with its proposed ionic nature. The co-ordination of the pyridine moiety can be inferred by the change in the ^{1}H NMR signals pattern. In the free ligand, in fact, the pyridine protons sequence is H_1, H_4, H_3, H_2 (from low fields to high fields), which is due to the anisotropic de-shielding effect of the C=N bond towards H_4 (Scheme 1) [12]. The co-ordination to the metal implies a rotation around the py-C(imine) bond, which places the imine nitrogen away from H_4, thus, leading to the sequence H_1, H_3, H_4, H_2. Moreover, the co-ordination of the ligand causes downfield shifts of 0.4 and 0.9 ppm for the imine and methyl protons, respectively, which are in favour of the involvement of the imine and amine nitrogens in the co-ordination. The methylene protons origin broad signals at about 4.2 and 3.2 ppm, probably because of the mobility of the alkyl bridge.

Complex **4** reacts with a stoichiometric amount of AgOTf in acetonitrile at room temperature, leading to the fast precipitation of silver chloride and to the isolation of the cationic complex **5**. The ^{1}H NMR spectrum is identical to that obtained for complex **4**, an this is a confirmation of the terdentate nature of the ligand in both complexes. The presence of an uncoordinated triflate anion is confirmed by the IR spectrum with a strong band centred at 1259 cm^{-1} [13].



Scheme 3.

3.2. Catalysis

All the prepared palladium complexes have been tested as catalysts in the hydrogenation of styrene and several acetylenic substrates at $P_{H_2} = 1$ atm and $T = 40\,^{\circ}C$. Complex **4** results completely inactive both in the hydrogenation of styrene and phenylacetylene; interestingly, no traces of palladium black have been detected. Diversely, complex **5** quickly decomposes under hydrogen atmosphere both with styrene and phenylacetylene, resulting in palladium black. Complexes **1** and **2** have been used as catalysts in the homogeneous hydrogenation of styrene and phenylacetylene. As can be inferred by the results collected in Table 1, the reactivity of the complexes is strongly influenced by the nature of the counter-ion: when the substrate is styrene, after 6 h of reaction the acetate complex leads to its complete hydrogenation (entry 1), whereas the chloride complex leads only to a 65% conversion (entry 2). This different reactivity can

Table 1
Hydrogenations catalysed by complexes **1** and **2**[a]

Entry	Complex	Substrate	Time (h)	Products	Conversion (%)
1	**2**	Styrene	6	100% ethylbenzene	100
2	**1**	Styrene	6	65% ethylbenzene	65
3	**2**	Phenylacetylene	5	58% styrene and 2% ethylbenzene	60
4	**1**	Phenylacetylene	5	20% styrene	20

[a] Solvent, THF; $P_{H_2} = 1$ atm; $T = 40\,^{\circ}$C.

be related to the better leaving group nature of the acetate, which can be a fundamental requirement for the substrate co-ordination. These results agree with previous studies on hydrogenation reactions catalysed by palladium(II) complexes containing hydrazonic terdentate ligands [8,9].

The hydrogenation of phenylacetylene proceeds with a good chemo-selectivity in the presence of both complexes (Table 1, entries 3 and 4) without releasing of palladium black. The unexpected faster hydrogenation of styrene (compared to that of the more co-ordinating phenylacetylene) is not easily explainable; one reason could be the formation of pollutant containing palladium agents deriving from a σ interaction between the alkyne and the catalysts, as already observed for other palladium(II) complexes [8,9]. However, no species different from the starting complexes have been recovered at the end of the reaction.

The catalytic activity of the complexes **1** and **2** towards the more encumbered substrates 1,2-diphenylacetylene and 4-octyne is negligible (after 24 h of reaction only 12% of the substrate has been hydrogenated to the *cis* product).

Table 2
Hydrogenation catalysed by complex **3**[a]

Entry	Substrate	Time (h)	Products	Conversion (%)
1	Phenylacetylene	5	45% styrene and 55% ethylbenzene	100
2	Diphenylacetylene	5	57% stylbene (*cis*) and 40% diphenylethane	97
3	4-octyne	5	85% 4-octene (*cis*)	85

[a] Solvent, *n*-hexane; $P_{H_2} = 1$ atm; $T = 40\,^{\circ}$C.

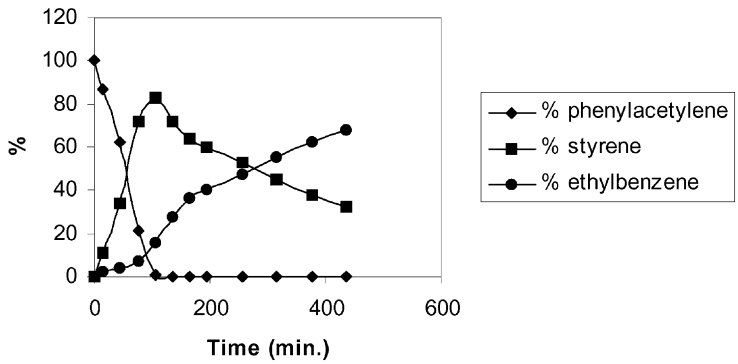


Fig. 1. Hydrogenation of phenylacetylene catalysed by complex **3** in heterogeneous conditions.

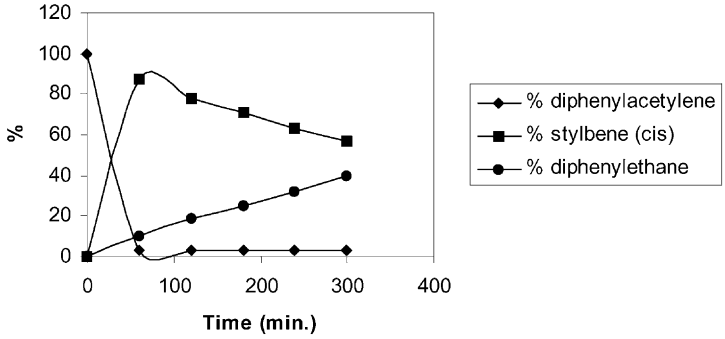


Fig. 2. Hydrogenation of diphenylacetylene catalysed by complex **3** in heterogeneous conditions.

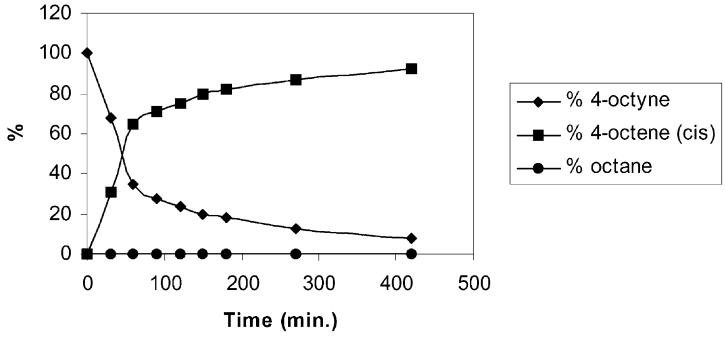


Fig. 3. Hydrogenation of 4-octyne catalysed by complex **3** in heterogeneous conditions.

The homogeneous nature of the process is confirmed by the chemo-selectivity of the process itself.

The trinuclear nature of complex **3** was thought to have a beneficial effect on the catalysis. Unfortunately, its complete insolubility has not enabled its use in homogeneous conditions; however, a good catalytic activity has been observed when **3** has been dispersed in *n*-hexane in the presence of a 100-fold excess of styrene, phenylacetylene, 1,2-diphenylacetylene or 4-octyne. The hydrogenation of styrene proceeds smoothly to ethylbenzene, while in the presence of acetylenic substrates a good or excellent chemo-selectivity has been observed, depending on the substrate. The results are collected in Table 2. The selectivity of the process promoted by complex **3** in the presence of alkynes is well evidenced by Figs. 1–3. The reactions proceed with the fast reduction of the triple bond to the corresponding *cis*-olefin and then continue with the slower reduction of the olefin to the corresponding saturated product. In any case, the hydrogenation of the olefin takes place only when the starting substrate has been almost completely consumed and the olefin percentage is higher than 80%. The highest selectivity has been found with the bulky 4-octyne: after 7 h of reaction, 92% of *cis*-octane is obtained and no traces of saturated product are present in solution (Table 2, entry 3).

4. Conclusions

A series of palladium(II) complexes containing trinitrogen ligands has been synthesised. In the new complexes **4** and **5**, the NNN ligand $\mathbf{L^2}$ behaves as tridentate, and the square planar co-ordination is completed by a chloride ion. All the complexes have been tested as catalysts in the hydrogenation of unsaturated C–C bonds. Although complexes **4** and **5** do not show

any catalytic activity neither with olefins nor with alkynes, the complexes **1**–**3**, containing ligand **HL[1]**, show interesting catalytic performances. Complexes **1** and **2** show a fair activity in the homogeneous hydrogenation of styrene and phenylacetylene, the activity being influenced by the nature of the counter-ion: a better living group nature corresponds to a faster reduction of the substrate. Worth noticing is the excellent activity shown by the extremely insoluble complex **3**: when dispersed in *n*-hexane in the presence of the substrate, a high chemo- and stereo-selective hydrogenation takes place.

The electronic and steric nature of the substrates influences the rate and the selectivity of the process: terminal or activated triple bonds (phenylacetylene and diphenylacetylene, Table 2, entries 1 and 2) are rapidly converted to alkenes (*cis* for diphenylacetylene). With internal less co-ordinating triple bond (4-octyne, Table 2, entry 3) the hydrogenating process is slower, but it occurs with a high selectivity to *cis*-alkene. In all cases, no palladium black has been formed during the hydrogenations.

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