ELSEVIER

www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 583 (1999) 94–105

Journal of Organometallic Chemistry

Palladium(II) complexes containing a P, N chelating ligand Part III. Influence of the basicity of tridentate hydrazonic ligands on the hydrogenating activity of unsaturated C–C bonds☆,☆☆

Paolo Pelagatti [a], Alessia Bacchi [a], Mauro Carcelli [a], Mirco Costa [c,*], Andrea Fochi [a], Patrizia Ghidini [a], Enrico Leporati [a], Maurizio Masi [b], Corrado Pelizzi [a], Giancarlo Pelizzi [a]

[a] *Dipartimento di Chimica Generale ed Inorganica, Chimica Fisica, Chimica Analitica, Università degli Studi di Parma, Viale delle Scienze 17/A, 43100 Parma, Italy*

[b] *Dipartimento di Chimica Fisica Applicata, Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133 Milano, Italy*

[c] *Dipartimento di Chimica Organica ed Industriale, Università degli Studi di Parma, Viale delle Scienze 17/A, 43100 Parma, Italy*

Received 2 July 1998; received in revised form 12 October 1998

Abstract

Several potentially tridentate hydrazonic ligands containing a PNO donor atom set were synthesised and used to prepare the corresponding acetato palladium(II) complexes. These were used as catalysts in the homogeneous hydrogenation of styrene and other unsaturated C–C bonds under mild conditions. Depending on the basicity of the hydrazonic nitrogen of the ligand, a different catalytic activity of the complexes was observed. This substantiates a heterolytic activation of the molecular hydrogen, which leads to the protonation of the ligand and formation of a palladium(II) hydride complex. Kinetic studies of the hydrogenation of styrene in methanol were performed, using complex **1a** as catalyst. A dependence, approximately of first order in hydrogen and catalyst concentrations and zero order in styrene concentration, was found. Two kinetic equations derived from a statistic processing are compared. The X-ray crystal structure of complex **1a** is also reported.

Keywords: Palladium; Hydrogenation; Homogeneous catalysis; Tridentate ligands; Kinetic; Mechanism

1. Introduction

Symmetric bidentate ligands such as diphosphines and N∩N chelating systems, have been extensively used both in synthesis of organometallic compounds [1] and homogeneous catalysis [2]. In the latter case, mechanistic studies have suggested that the cleavage of a coordinating M–P or M–N bond is a crucial step in the catalytic cycle if not the rate determining step [3]. The strong chelating effect played by diphosphines towards soft metals, can lead to a slowing down of the catalytic reaction, whereas N∩N systems, containing donors with a higher hard character, are often not able to prevent the decomposition of the complex during the reaction. Good results, in terms of robustness and efficiency of the catalysts, have been obtained with complexes of asymmetric bidentate ligands, such as PN [4], NS [5], NO [6] and PO [7], containing both a soft donor and a hard one [8]. Only in recent years has some interest been directed to the study of asymmetric tridentate ligands [9]. These systems can potentially behave like tridentate as well as bidentate ligands, according to the concept of hemilability introduced by Jeffrey and Rauchfuss [8d], and are expected to offer new catalytic properties for the corresponding complexes, like a bet-

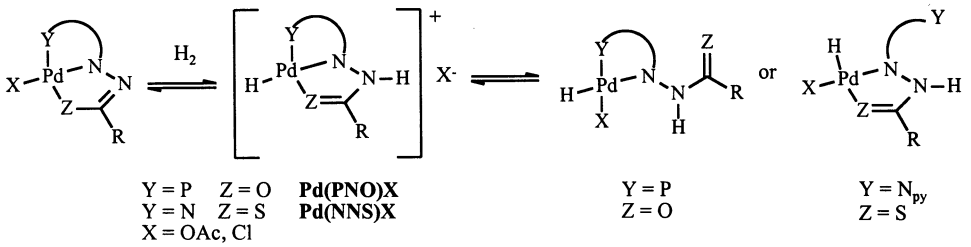
☆ Dedicated to Professor A. Ceccon on the occasion of his 65th birthday.

☆☆ For Part II see [15b].

* Corresponding author. Fax: +39-521-905557.

E-mail address: costa@ipruniv.cce.unipr.it (M. Costa)

0022-328X/99/$ - see front matter
PII: S0022-328X(99)00109-6



Scheme 1. Postulated heterolytic activation of the molecular hydrogen with PNO and NNS systems.

ter chemoselective or stereoselective control of the reaction.

The hemilabile behaviour of these ligands has been well demonstrated in some works concerning tridentate systems of the type PNN [10], PON or POP [11], PNO [9g], NNS [12] and is invoked as responsible of the observed catalytic activity of the complexes.

As part of our research, we have been studying for some years the catalytic application of palladium(II) complexes with tridentate ligands of formula Pd(L)X (L = tridentate ligand, X = CH_3CO_2, Cl, I) in the homogeneous hydrogenation of alkenes and alkynes under mild conditions, with particular regard to the chemoselectivity from triple to double bond. Our studies have concerned several systems containing different donor atom sets, like NNO [13], NNS [14], PNO or PNS [15].

The nature of the donor atoms stabilising the complexes in an hydrogen atmosphere appeared to be of fundamental importance. Thus, when using complexes containing no soft atoms (NNO), the formation of black palladium was observed rapidly and the decomposition of the complexes was complete in a few minutes. On the contrary using PNS complexes, containing two soft donors, no catalytic activity was observed owing to the strong chelating effect exerted by the ligand on the metal centre. A good compromise was reached with PNO and NNS systems, where the presence of a soft donor (P or S) stabilises the complexes during the reaction and the presence of a hard donor (O or N) allows the coordination of an unsaturated substrate by breaking of a Pd–O or a Pd–N coordinating bond.

A second central point coming out from our research concerns the nature of the counterion bonded to palladium in ruling the chemoselectivity of the process. In fact, X can further control the accessibility to the metal for an incoming molecule (substrate or molecular hydrogen). Thus, when X is a good leaving group, like an acetate, it can be replaced both by an olefin and an acetylenic molecule, forming a π-bond. Instead, when X has a stronger coordinating capability, like in the case of a chloride atom, only a triple bond can coordinate on the metal; lastly, the high affinity of the iodine atom for palladium(II) causes the complete inertness of the iodide complexes.

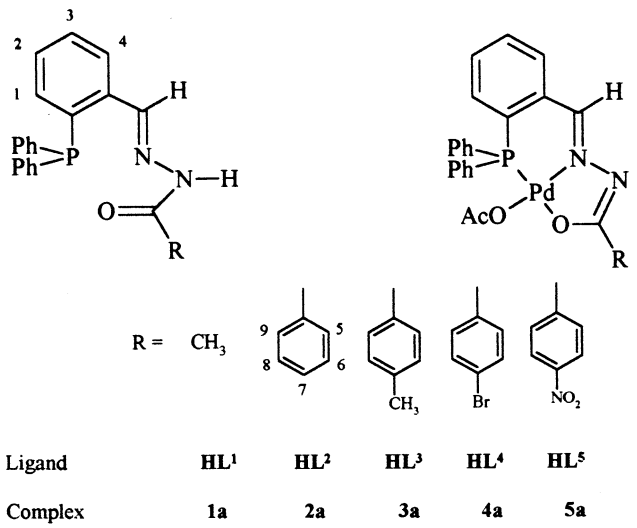
The presence, in the ligands, of a basic site represented by a hydrazonic nitrogen, prompted us to advance a heterolytic way of activation of the molecular hydrogen [16], with protonation of the ligand and formation of a cationic hydride complex, as shown in Scheme 1.

With the aim to confirm this hypothesis and get more detailed mechanistic information on the catalytic behaviour of the complexes, we synthesised several acetate palladium(II) complexes containing hydrazonic tridentate ligands, with different basicity changing the R group of the hydrazonic arm (Scheme 2, Table 3). Here we report their synthesis, characterisation and a study of their catalytic activity in the homogenous hydrogenation of styrene and other unsaturated substrates under mild conditions. A kinetic study of the reaction was carried out using complex **1a**. The crystalline structure of complex **1a** is also reported.

2. Experimental details

2.1. Preparation

All reactions were carried out under nitrogen. The solvents were dried according to literature methods and



Scheme 2. Schematic presentation of ligands HL^1–HL^5 and acetate palladium(II) complexes **1a**–**5a**.

Table 1
Summary of crystal data, intensity collection and refinement

Compound	**1a**·H_2O
Formula	$C_{23}H_{23}N_2O_4PPd$
Molecular weight	528.82
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	9.438(3)
b (Å)	13.734(5)
c (Å)	9.364(3)
α (°)	103.08(2)
β (°)	105.91(2)
γ (°)	74.03(2)
V (Å^3)	1107.2(7)
Z	2
$D_{calc.}$ (g cm^{-3})	1.586
Radiation	Mo–Kα
μ (cm^{-1})	9.426
Reflections measured	5340
Reflections unique	5340
Reflections observed ($F_o > 4\sigma(F_o)$)	4128
Refined parameters	286
R_1 for observed data	0.0628
wR_2 for all data	0.1777

stored under inert atmosphere. 2-(diphenylphosphino)benzaldehyde was purchased from Aldrich-Chemie. The hydrazidic systems were synthesised by the reaction between hydrazine monohydrate (98%, Fluka) and the corresponding ester.

Elemental analysis (C, H, and N) were performed by using a Carlo Erba Mod. EA 1108 apparatus.

Infrared spectra were recorded with a Nicolet 5PCFT-IR spectrophotometer in the 4000–400 cm^{-1} range by using KBr disks.

^{1}H-NMR spectra were obtained on a Bruker 300 FT spectrometer using $SiMe_4$ as internal standard. GC analysis were performed on a DANI HP 3800 flame-ionisation gas-chromatograph (OV 101 on CHP column). MS spectra (CI, methane) were recorded on a Finnigan SSQ 710 spectrometer.

2.2. Preparation of the ligands

A total of 0.100 g (0.345 mmol) of 2-(diphenylphosphino)benzaldehyde were dissolved in 10 ml of dichloromethane and some drops of glacial acetic acid were added; an equimolar amount of the corresponding hydrazide, dissolved in 30 ml of methanol, was added and the mixture was refluxed till the complete bleaching of the solution. The progress of the reaction was followed by TLC (SiO_2, dichloromethane/hexane: 8/2) monitoring the disappearance of the aldehyde. At the end of the reaction the solution was concentrated by rotavapor and 20 ml of diethyl ether were added before cooling at −20°C for a night. A white solid was filtered and washed with some millilitres of diethyl ether and finally dried in a vacuum.

HL[1]: m.p.: 205–206°C. Yield: 71%. MS, m/z (relative intensity): 347([M + 1]$^+$, 100), 288(87). Anal. Calc. $C_{21}H_{19}N_2OP$: C, 72.82; H, 5.52; N, 8.09%. Found: C, 72.85; H, 5.50; N, 8.05%. FTIR (cm^{-1}): ν(CN) 1598w; ν(CP) 1433. ^{1}H-NMR ($CDCl_3$): δ7.41–7.21 (m, 14H, Ph); 2.23 (s, 3H, CH_3).

HL[3]: m.p.: 217–219°C. Yield: 83%. MS, m/z (relative intensity): 423([M + 1], 100), 288(45). Anal Calc. $C_{27}H_{23}N_2OP{\cdot}CH_3OH$: C, 73.25; H, 5.32; N, 6.38%. Found: C, 73.29; H, 5.39; N, 6.36%. FTIR (cm^{-1}): ν(CN) 1623w; ν(CP) 1434w. ^{1}H-NMR ($CDCl_3$): δ7.74 (d, 2H, H_5–H_9, J(*ortho*) 8 Hz); 7.78–6.89 (m, 17H, Ph); 2.37 (s, 3H, CH_3).

HL[4]: m.p.: 207–210°C. Yield: 80%. MS, m/z (relative intensity): 488([M$^-$], 100). Anal. Calc. $C_{26}H_{20}BrN_2OP$: C, 64.08; H, 4.14; N, 5.75%. Found: C, 64.19; H, 4.20; N, 5.86%. FTIR (cm^{-1}): ν(CN) 1591w; ν(CP) 1434w. ^{1}H-NMR ($CDCl_3$): δ7.73 (d, 2H, H_5–H_9, J(*ortho*) 8 Hz); 7.50 (d, 2H, H_6–H_8, J(*ortho*) 8 Hz); 7.42–6.88 (m, 15H, Ph).

HL[5]: m.p.: 112–115°C. Yield: 86%. MS, m/z (relative intensity): 453([M$^-$], 100). Anal. Calc. $C_{26}H_{20}N_3O_3P$: C, 70.35; H, 5.47; N, 17.56%. Found: C, 70.66; H, 5.54; N, 17.62%. FTIR (cm^{-1}): ν(CN) 1602w; $\nu(NO_2)_a$ 1523vs; ν(CP) 1434w; $\nu(NO_2)_s$ 1346vs. ^{1}H-NMR ($CDCl_3$): δ8.22 (d, 2H, H_6–H_8, J(*ortho*) 8.2 Hz); 8.03 (d, 2H, H_5–H_9, J(*ortho*) 8 Hz); 7.37–6.87 (m, 13H, Ph).

2.3. Preparation of the acetato palladium(II) complexes ***1a***, ***3a***–***5a***

A total of 0.100 g of the ligand were dissolved in 10 ml of dichloromethane obtaining a colourless solution. An equimolar amount of $Pd(CH_3CO_2)_2$, dissolved in 25 ml of acetonitrile, was dropped into the ligand solution and the resulting yellow mixture was stirred for 2 h at room temperature. At the end of the reaction the solvent was partially removed by vacuum pump and 15 ml of diethyl ether were added before cooling at −20°C for a night. A yellow microcrystalline product was filtered and washed with some millilitres of diethyl ether then dried in vacuum.

1a: m.p.: 249–252°C (decomp.). Yield: 83%. Anal. Calc. $C_{23}H_{21}N_2O_3PPd$: C, 54.08; H, 4.14; N, 5.48%. Found: C, 54.05; H, 4.16; N, 5.45%. FTIR (cm^{-1}): $\nu(OCO)_a$ 1631s; ν(CN) 1560vw; ν(CP) 1433s; $\nu(OCO)_s$ 1313vs. ^{1}H-NMR ($CDCl_3$): δ7.69–7.35 (m, 15H, Ph); 2.14 (s, 3H, CH_3); 1.61 (s, 3H, CH_3CO_2).

3a: m.p.: 270–271°C (decomp.). Yield: 75%. Anal. Calc. $C_{29}H_{25}N_2O_3PPd{\cdot}2H_2O$: C, 55.92; H, 4.69; N,

4.50%. Found: C, 56.00; H, 4.55; N, 4.70%. FTIR (cm^{-1}): $\nu(OCO)_a$ 1623vs; $\nu(CN)$ 1583w; $\nu(CP)$ 1435m; $\nu(OCO)_s$ 1312s. ^{1}H-NMR (d_6-dmso): δ8.02 (d, 2H, H_5–H_9, $J(ortho)$ 8.1 Hz); 7.14 (d, 2H, H_6–H_8, $J(ortho)$ 8.1 Hz); 7.73–7.35 (m, 14H, Ph); 2.36 (s, 3H, CH_3); 1.64 (s, 3H, CH_3CO_2).

4a: m.p.: 259–259.8°C (decomp.). Yield: 79%. Anal. Calc. $C_{28}H_{22}BrN_2O_3PPd$: C, 51.60; H, 3.40; N, 4.30%. Found: C, 51.80; H, 3.46; N, 4.53%. FTIR (cm^{-1}): $\nu(OCO)_a$ 1624vs; $\nu(CN)$ 1589w; $\nu(CP)$ 1436m; $\nu(OCO)_s$ 1312s. ^{1}H-NMR (d_6-dmso): δ8.01 (d, 2H, H_5–H_9, $J(ortho)$ 8.1 Hz); 7.74–7.33 (m, 16H, Ph); 1.65 (s, 3H, CH_3CO_2).

5a: m.p.: 290–292°C (decomp.). Yield: 87%. Anal. Calc. $C_{28}H_{22}N_3O_5PPd$: C, 54.42; H, 3.58; N, 6.80%. Found: C, 54.63; H, 3.64; N, 6.78%. FTIR (cm^{-1}): $\nu(OCO)_a$ 1625s; $\nu(CP)$ 1436m; $\nu(OCO)_s$ 1312m. ^{1}H-NMR ($CDCl_3$): δ8.16 (d, 2H, H_5–H_9, $J(ortho)$ 8.9 Hz); 7.74–7.39 (m, 14H, Ph); 1.66 (s, 3H, CH_3CO_2).

2.4. Determination of the log β of the ligands

The procedure was equivalent to that earlier reported [15b]. The ligands were dissolved in a water/methanol solution (80/20%, v:v). The range of concentration of the various ligands in the spectrophotometric titration was $2.6922 \times 10^{-5} - 8.1882 \times 10^{-5}$ mol l^{-1}.

2.5. Structure

X-ray intensity data were collected using a Philips PW100 diffractometer. Details of the experimental conditions, crystal data, data collection and crystal refinement are given in Table 1. Intensities were corrected for Lorentz and polarisation effects. The intensity of one reflection was monitored every 100 reflections during data collection to check for crystal decay or loss of alignment. No loss of intensity was observed.

The structure was solved by direct methods and refined by full-matrix least-squares based on F^2. Anisotropic vibration was allowed for all non-hydrogen atoms. All hydrogen atoms were included at calculated positions, riding on their carrier atoms, with the exception of H7 and those belonging to the water molecule, which were located in ΔF maps, and refined isotropically.

Calculations were performed on a Digital Alpha255 workstation using the program packages SIR97 [17], SHELXL97 [18], PARST [19] and ZORTEP [20].

Final atomic coordinates are listed in Table 4 and a selection of bond distances and angles is shown in Table 5.

2.6. Catalysis

All manipulations were carried out under purified dry nitrogen by use of standard Schlenk techniques. Solvents were dried following literature methods and stored under nitrogen. The hydrogenating apparatus has already been described [14,15]. The progress of the reaction was followed by GC. The stirrer was operated in such manner that there was no limitation due to diffusion control. In order to use the initial rates method in the calculations we considered conversions up 20%. Hydrogen pressures inferior to 1 atm were obtained mixing, at constant pressure and temperature, exact volumes of hydrogen and nitrogen in a gas burette and keeping the gases in contact for 12 h. The solubility of hydrogen in methanol was considered to be constant for every run. The concentration of hydro-

Table 2
Selected IR and NMR (ppm, solvent: $CDCl_3$) data for ligands and complexes

Name	IR (cm^{-1})				^{1}H-NMR		^{31}P-NMR
	ν(NH)	ν(CO)	AMIDE II	AMIDE III	δ(NH)	δ(CH=N)	δ
HL^1	3192_{br}	1678_{vs}	1477_s	1328_s	8.75_s	8.37_d[4.3]	−14
HL^2	3220_{br}	1652_{vs}	1550_s	1285_s	9.49_s	8.95_d [c]	−12.5
HL^3	3218_m	1646_{vs}	1558_m	1320_m–1280_m	9.55_s	8.90_d [3.5]	−19.5
HL^4	3221_m	1650_{vs}	1555_w	1301_m–1285_w	9.64_s	8.97_d [3.5]	−15.8
HL^5	3211_{br}	1657_{vs}	1557_m	1289_m	10.23_s	9.04_d [4.9]	−15.8
1a	–	–	1505_{vs}	1380_s	–	8.25_d [3.5]	28.4
2a	–	–	1522_{vs}	1392_s	–	8.10_d [3.5]	28.6
3a	–	–	1505_{vs}	1384_s–1360_{vs}	– [d]	8.23_d [3.5]	33.2
4a	–	–	1506_s–1480_s	1383_s–1356_{vs}	–	8.24_d [3.5]	28.5
5a	–	–	1529_s [a]	1339_{vs}–1312_s [b]	–	8.31_m [c,e]	28.6

[a] Contribute due to $\nu(NO_2)_{as}$.
[b] Contribute due to $\nu(NO_2)_s$.
[c] J(PH) could not be determined.
[d] Solvent, d_6-dmso.
[e] Overlapping with the signals due to H_6–H_8.

Table 3
Protonation constants ($\log \beta_{11}$) of hydrazonic nitrogen for the different ligands from absorbance data (230–430 nm) [a]

Ligand	**HL[1]**	**HL[2]**	**HL[3]**	**HL[4]**	**HL[5]**
$\log \beta_{11}$	13.13(3)	12.34(1)	12.51(5)	12.13(2)	11.27(1)
U [b]	3.730×10^{-3}	7.145×10^{-2}	1.545×10^{-1}	8.889×10^{-3}	2.236×10^{-3}
σ_{tot} [b]	1.629×10^{-3}	8.436×10^{-3}	1.227×10^{-2}	2.352×10^{-3}	1.362×10^{-3}
N_p	1809	1407	1368	2010	1608
pH (range)	11.40–12.77	7.15–12.85	7.64–12.46	10.14–12.40	10.19–12.19

[a] Temperature, 25°C; ionic strength (I), 0.1 mol dm^{-3} (KCl).
[b] $\sigma_{tot} = [\Sigma w_i(A_c - A_o)^2/(NBA(NUMPH - JQ) - NCV)]^{1/2}$; $U = [\Sigma w_i(A_c - A_o)^2]$ where NBA is the number of wavelengths (λ); NUMPH is the number of solutions; JQ is the number of ε to be calculated; NCV is the number of protonation constant to be refined; w_i is the unit weight; and N_p is the number of points data used in the refinement.

gen was determined as a function of temperature and hydrogen pressure using the empirical equation $\ln(H/\text{MPa}) = 122.3 - 4815.6(\text{T/K}) - 17.5\ln(\text{T/K}) + 1.4 \times 10^{-7}(P/\text{Pa})$ [21], where H is the Henry's law constant and P is the partial pressure of hydrogen.

At the end of the reaction the solvent was partially removed under vacuum and diethyl ether was added in order to precipitate the catalyst, the nature of which was confirmed by FTIR.

2.7. Hydrogenation of styrene, butyl-acrylate and methyl-crotonate

The experimental conditions for complex **1a** are as follows: 0.010 g of **1a** (0.020 mmol) and an appropriate amount of substrate were dissolved in an adequate volume of methanol, in order to have $[\mathbf{1a}] = 1.740 \times 10^{-3}$. The solution was then thermostated at 40°C. At the end of the reaction the starting complex was recovered unchanged.

2.8. Hydrogenation of 1,5-cyclooctadiene(cod), 1-octene and 1,2-diphenylacetylene

The procedure was the same to that reported above, except for the solvent, which in this case was THF. At the end of the reaction the starting complex was recovered unchanged.

3. Results and discussion

3.1. Synthesis of the ligands and complexes

Ligand **HL[2]** was previously synthesised by condensation between 2-(diphenylphosphino)benzaldehyde and benzoylhydrazine [15a], in the presence of glacial acetic acid. Using the appropriate hydrazidic systems, it was possible to isolate the ligands **HL[1]** and **HL[3]**–**HL[5]** in a similar way. They proved to be fairly insensitive towards oxidation in the solid state but, in solution, some traces of the oxidation products were observed within 2 days. The analysis of the IR and NMR (^{1}H and ^{31}P) data (Table 2) highlights the high similarity existing between the different ligands: IR spectra show a strong band at about 1650 cm^{-1}, corresponding to the stretching of the C=O group and a broad band at about 3200 cm^{-1} due to the stretching of the N–H bond. The hydrazonic chain originates, in all cases, two strong bands at about 1500–1550 cm^{-1} and 1300 cm^{-1} belonging to the AMIDE II and AMIDE III systems,

Table 4
Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^4$) (one third trace of the diagonalised matrix), with estimated S.D. in parentheses for compound **1a**·H_2O

Atom	X/a	Y/b	Z/c	U_{eq}
Pd	10936.2(4)	2495.1(3)	9241.8(4)	291(2)
P	8617(1)	2612.2(9)	7846(1)	255(4)
O1	12946(4)	2320(3)	10847(4)	375(14)
O2	11788(4)	1394(3)	7644(4)	383(14)
O3	12435(5)	2661(3)	7055(5)	521(18)
O4	11620(7)	4433(4)	15728(6)	714(25)
N1	10312(5)	3578(3)	10882(5)	310(15)
N2	11425(5)	3581(4)	12246(5)	419(18)
C1	7404(5)	3855(3)	8311(5)	278(16)
C2	6045(6)	4152(4)	7294(6)	389(19)
C3	5055(6)	5084(4)	7577(7)	443(22)
C4	5429(6)	5743(4)	8897(7)	407(21)
C5	6775(6)	5467(4)	9938(6)	369(19)
C6	7776(5)	4519(3)	9669(5)	292(17)
C7	9126(6)	4324(4)	10894(6)	327(18)
C8	12694(6)	2903(5)	12080(6)	431(22)
C9	13977(7)	2819(7)	13464(8)	624(30)
C10	7820(5)	1668(3)	8262(5)	281(16)
C11	6403(6)	1905(4)	8568(6)	377(20)
C12	5884(7)	1177(5)	8978(7)	473(24)
C13	6768(7)	201(5)	9029(7)	509(26)
C14	8170(7)	−60(4)	8678(7)	473(24)
C15	8709(6)	672(4)	8310(7)	396(20)
C16	8437(6)	2401(4)	5818(6)	302(17)
C17	8146(7)	1502(4)	4935(6)	427(22)
C18	8103(8)	1332(5)	3415(7)	566(27)
C19	8372(7)	2067(5)	2788(7)	524(25)
C20	8650(7)	2967(5)	3681(7)	517(26)
C21	8699(7)	3137(5)	5190(6)	422(21)
C22	12345(7)	1764(4)	6840(6)	416(21)
C23	12920(12)	1012(6)	5586(10)	867(46)

Table 5
Selected bond distances (Å) and angles (°) in compound **1a**·H_2O

Bond lengths (Å)			
Pd–P	2.204(1)	O2–C22	1.280(9)
Pd–O1	2.065(3)	O3–C22	1.225(8)
Pd–O2	2.034(4)	N1–N2	1.414(6)
Pd–N1	1.974(4)	N1–C7	1.293(6)
P–C1	1.809(4)	N2–C8	1.322(7)
O1–C8	1.287(7)	C1–C6	1.407(6)
		C6–C7	1.470(6)
Bond angles (°)			
P–Pd–O1	169.1(1)	Pd–N1–C7	131.4(4)
P–Pd–O2	91.3(1)	N2–N1–C7	114.9(4)
P–Pd–N1	94.0(1)	N1–N2–C8	111.4(5)
O1–Pd–O2	94.4(1)	P–C1–C6	122.4(3)
O1–Pd–N1	80.5(1)	C1–C6–C7	126.8(5)
O2–Pd–N1	174.4(1)	N1–C7–C6	127.7(5)
Pd–P–C1	111.6(1)	O1–C8–N2	126.1(6)
Pd–O2–C22	111.8(4)	O1–C8–C9	117.1(5)
Pd–N1–N2	113.4(3)		

whereas the ν(C=N) is visible with a weak signal at about 1600 cm^{-1}. In the IR spectra of **HL**[5], the two strong bands at 1523 and 1346 cm^{-1}, derive from the asymmetric and symmetric stretching of the NO_2 group, respectively.

Hydrazonic proton resonates as a broad singlet in the region 8.75–10.23 ppm, where the latter value is that belonging to **HL**[5], pointing out the deshielding effect played by the nitro group. The iminic proton resonates as a doublet at about 8.9 ppm with a J(P–H) of about 4 Hz, a characteristic value for phosphino–imino ligands similar to those here reported [10,22].

The phosphorous atom generates a singlet in the ^{31}P-NMR in the region $-12.5/-19.5$ ppm. The protonation constants of the hydrazonic nitrogen for the different ligands are collected in Table 3.

HPNO ligands **HL**[1]–**HL**[5] reacted with $Pd(CH_3CO_2)_2$ leading to the formation of the corresponding Pd(PNO)(OAc) complexes. The reaction occurred with deprotonation of the ligand resulting in formation of CH_3CO_2H. In all cases the hydrazones coordinate in a tridentate mode, through the phosphorous atom, the iminic nitrogen and the oxygen donor, the fourth coordination site being satisfied by an acetate group.

The involvement of the phosphorous atom in the coordination is proved by the strong deshielding observed for the singlet in the ^{31}P-NMR spectrum of the complexes (Table 2).

The anionic nature of the ligands is confirmed by the absence, both in the IR and ^{1}H-NMR spectra, of the signals generated by the N–H group; consequently the disappearance of the C=O stretching points out the presence of a Pd–O coordination. The coupling between the iminic proton and the phosphorous atom is still observable in the ^{1}H-NMR spectra of the complexes. The typical IR signals for an acetate monodentate are present in the IR spectra of **1a**–**5a** [23].

1a–**4a** are stable both in solution and in the solid state whereas **5a**, after some days in solution at room temperature, releases some traces of black palladium.

3.2. Structure

Compound **1a**·H_2O is shown in Fig. 1, along with the labelling scheme.

The complex molecule contains a deprotonated hydrazonic ligand, behaving as terdentate PNO donor. This gives rise to one five and one six membered chelation rings.

The NNCO chelation system is planar within 0.010 Å, while the PCCCN one is planar within 0.073 Å. The Pd atom is out of the above planes by 0.19 and 0.54 Å, respectively. The two chelate rings form a dihedral angle of 20.4°. The distorted square planar coordination is completed by an acetate molecule acting as monodentate (Pd–O2 = 2.034(4) Å), with the second oxygen at a distance of 2.867(6) Å from the metal atom. The most relevant distortion in the square planar geometry is evident in the *trans* angle P–Pd–O1 (169°), and in the non perfect planarity of the coordination polyhedron (maximum deviation from planarity is 0.15 Å for N1).

The distances among the donor atoms and Pd fall in the range of distances observed in other similar

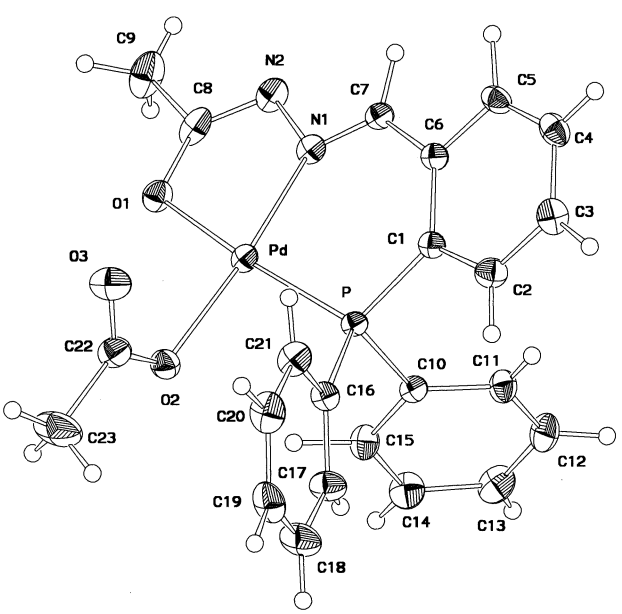


Fig. 1. Perspective view of compound **1a**·H_2O. Thermal ellipsoids are drawn at the 50% probability level.

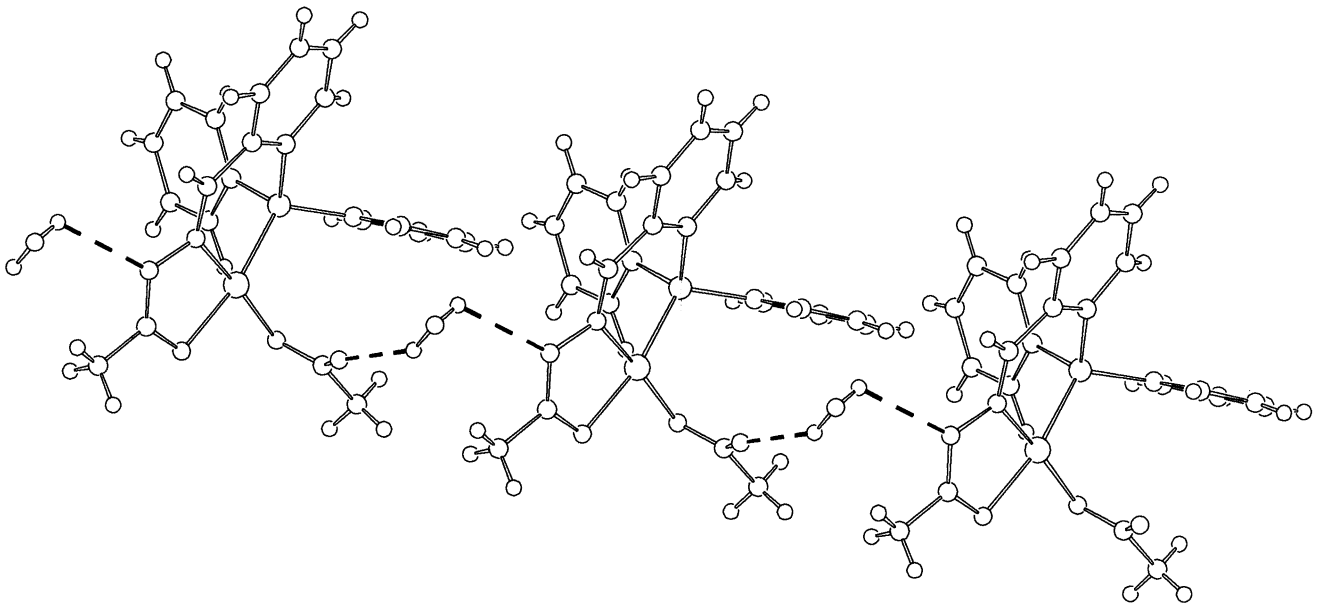


Fig. 2. Crystal packing of **1a**·H_2O. Waters bridge complex molecules in chains along z-axis.

compounds [13,15]. The hydrazonic core of the ligand, excluding the two phenyl groups, is not planar as already put in evidence through the observation of chelate rings (maximum deviation from planarity is 0.41 Å for O1).

The complex crystallises with a molecule of water. This seems to be important in the packing of the compound due to the formation of the hydrogen bonds: O4–H…N2 (O4…N2 = 3.178(7) Å, O4–H…N2 = 128.6(4)°) and O4–H…O3(x, y, $z+1$) (O4…O3 = 2.806(7) Å, O4–H…O3 = 148.3(3)°). These contacts lead to the formation of a polymeric chain along the z-axis (Fig. 2).

3.3. Catalysis

All the acetato palladium(II) complexes were tested as catalysts in the homogeneous hydrogenation of styrene, at 40°C, 1 atm of hydrogen pressure and methanol as solvent. The reaction times necessary for the complete conversion of styrene to ethylbenzene in the presence of **1a**–**5a** as catalysts, are summarised in Table 6.

Hydrogenation of other unsaturated substrates, such as butyl acrylate, methyl crotonate, 1,5-cyclooctadiene (*cod*), 1-octene and diphenylacetylene was carried out in the presence of complex **1a**; the results are collected in Table 7. Terminal activated C–C double bonds and a chelating system like *cod* gave the best results.

Complexes **1a**–**5a** showed to be sufficiently robust during the catalysis. Black palladium only became visible when the complexes were kept in contact with hydrogen without any substrate or for very long reaction times ($\geq$ 48 h).

The results collected in Table 6 point out that the hydrogenating activity of the acetate complexes is strongly influenced by the ligand basicity, the latter being determined by the nature of R. Indeed when R=CH_3, the hydrogenation of styrene was complete in 1.5 h only, whereas when R=p-NO_2–C_6H_4, even after 72 h of reaction, 21% of styrene was still present in solution. Expressing the catalytic activity of the acetato complexes as the time required for the complete conversion of styrene to ethylbenzene, and considering the trend of basicity of the ligands, it is possible to evidence a correlation between these two parameters, as shown in Fig. 3.

Thus, to a higher ligand basicity corresponds a better catalytic activity of the complex and this finding agrees with a heterolytic cleavage of the molecular hydrogen, as shown in Scheme 1 [16]. However the application of the Hammet relation to these data did not give a good linear correlation.

Since complex **1a** was the most active catalyst in the hydrogenation of styrene, it was chosen in order to carry out a kinetic study of this reaction. The conver-

Table 6
Hydrogenation of styrene in the presence of **1a**–**5a** as catalysts [a]

Complex	**1a**	**2a**	**3a**	**4a**	**5a** [b]
Reaction time (h)	1.5	13	9	10	>72

[a] T, 40°C; P_{H_2}, 1 atm, [cat], 1.740×10^{-3}; [styrene], 1.740×10^{-1}; solvent, methanol.

[b] After 72 h, 21% styrene and 79% ethylbenzene.

Table 7
Results for the hydrogenation of different substrates using **1a** as catalyst [a]

Substrate	Time (h)	Conversion (%)	Product (% yield)
Butyl acrylate [b]	5	100	Butyl propionate (100)
Methyl crotonate [b]	24	35	Methyl butyrate (35)
cod [c]	24	93	Cyclooctene (90) Cyclooctane (3)
1-Octene [c]	24	80	Octane (45) *trans*-2-Octene (25) *cis*-2-Octene (5)
Diphenylacetylene [c]	6.5	98	*trans*-Stilbene (6) Diphenylethane (92)

[a] T, 40°C; P_{H_2}, 1 atm; [**1a**], 1.740×10^{-3}; [substrate], 0.261.
[b] Solvent, methanol.
[c] Solvent, THF; for 1-octene the residual 5% is due to other isomerisation products.

sions of styrene to ethylbenzene versus time were measured as a function of hydrogen pressure from 0.125 to 1 atm, at 40°C. The concentrations of styrene and catalyst were 0.300 M and 1.740×10^{-3} M, respectively. Ethylbenzene yields versus time at 40°C were obtained at different styrene concentrations (from 0.300 to 0.600 M) using a constant catalyst concentration (1.740×10^{-3} M) and a constant hydrogen pressure (1 atm). The effect of catalyst concentration (from 0.870×10^{-3} to 3.480×10^{-3} M) on rate at 40°C was determined at a constant styrene concentration (0.300 M) and a constant hydrogen pressure (1 atm). The conversions to ethylbenzene versus time were carried out at three different temperatures (30, 40 and 50°C) at constant catalyst (1.740×10^{-3} M) and styrene (0.300 M) concentrations and at constant hydrogen pressure (1 atm).

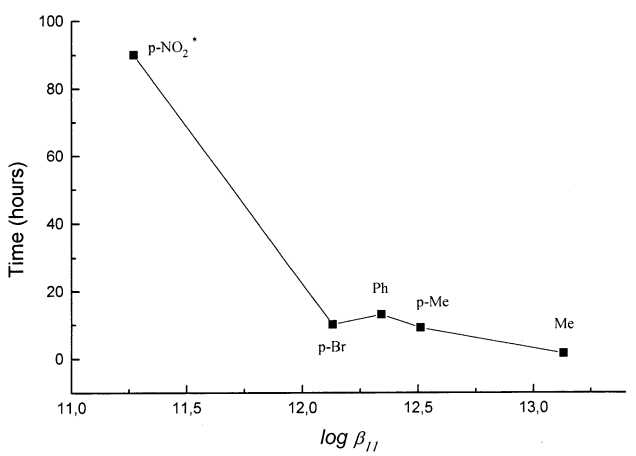


Fig. 3. Correlation between the protonation constants of the free ligands and the reaction time required for the complete conversion of styrene to ethylbenzene, in the presence of **1a**–**5a** as catalysts. * Extrapolated value.

A total of 72 experimental points were considered for the kinetic parameters evaluation. The estimation of the rate constant parameters were performed on the base of the integral method [24]. They were directly fitted above the experimental concentrations instead of on the reaction rate calculated through the incremental ratio. Accordingly, the material balances for styrene and ethylbenzene were written as follows:

$$-\frac{\mathrm{d[styrene]}}{\mathrm{d}t} = \frac{\mathrm{d[ethylbenzene]}}{\mathrm{d}t} = r([\text{styrene}], [\text{ethylbenzene}], [\text{cat}], [\mathrm{H_2}], \mathrm{T}, \xi) \quad (1)$$

where $\xi = (\alpha, \beta, \gamma, k_1, k_2, \ldots)$ the vector of the kinetic parameters [25].

As a result the overall kinetic equation was

$$r = A\exp(-E_a/\mathrm{RT})\ [\mathbf{1a}]^{1.38}\ [\mathrm{H_2}]^{1.03}\ [\text{styrene}]^{0.30} \quad (2)$$

The achieved styrene hydrogenation rate exhibits approximately a first order dependence on hydrogen and catalyst concentrations and a zero order dependence on styrene concentration. The rate of styrene hydrogenation increases with an increase of the temperature. The activation energy $E_a = 10.05 \pm 0.01$ kcal mol^{-1} was obtained by the Arrhenius equation

$$k = A\ \exp(-E_a/\mathrm{RT}) \quad (3)$$

where the pre-exponential factor $A = 2.5 \times 10^9$ mol^{-1} l s^{-1}. From the transition state theory, the kinetic constant k can be expressed as

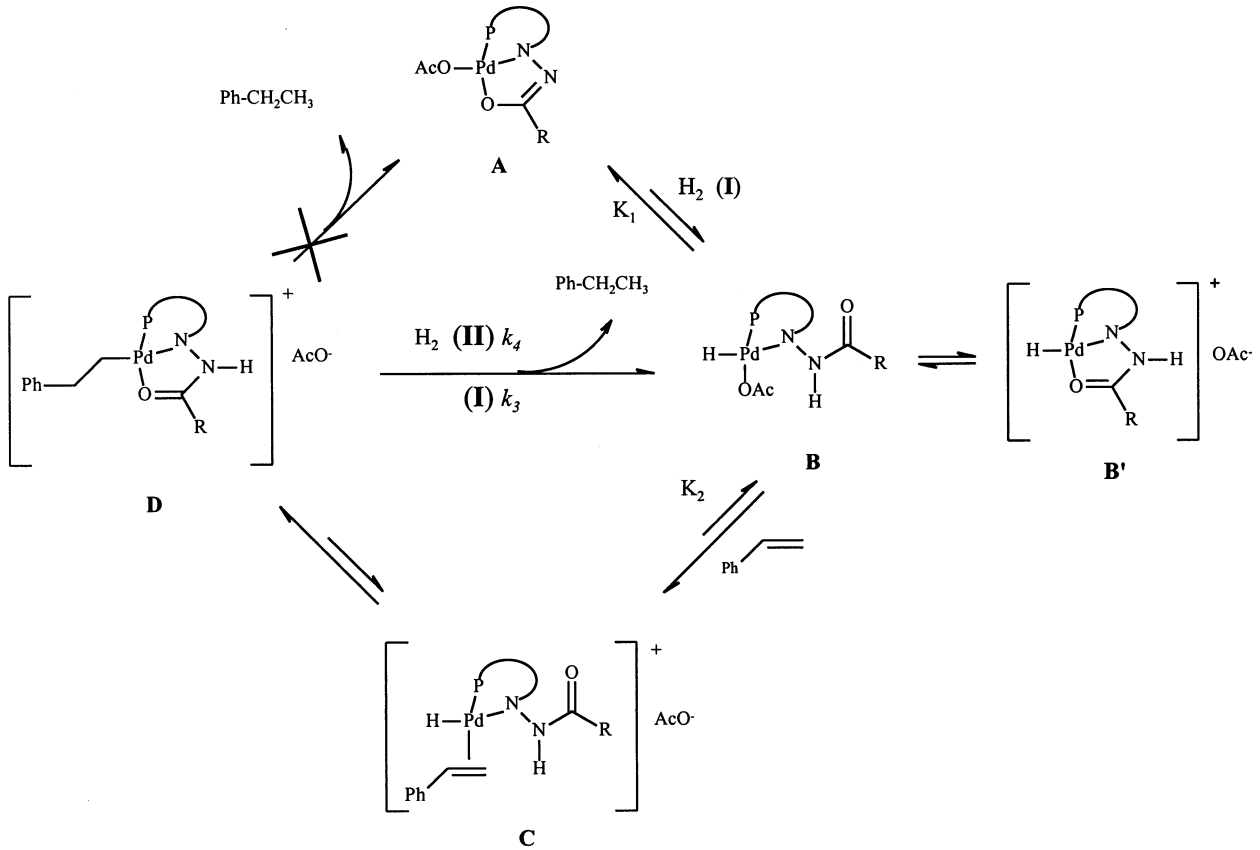
$$k = \frac{K_B \mathrm{T}}{h} \mathrm{e}^{-\frac{\Delta H^{\neq}}{\mathrm{RT}} + \frac{\Delta S^{\neq}}{\mathrm{R}}} \quad (4)$$

The standard enthalpy ($\Delta H^{\neq}$) and entropy ($\Delta S^{\neq}$) of activation were obtained from the Eyring equation

$$\ln(k'/\mathrm{T}) = \ln(K/h) + (\Delta S^{\neq}/\mathrm{R}) - (\Delta H^{\neq}/\mathrm{RT}) \quad (5)$$

where k' is the rate constant at different temperatures. The values were $\Delta H^{\neq} = 9.34 \pm 0.01$ kcal mol^{-1} and $\Delta S^{\neq} = -17.56 \pm 0.03$ cal mol^{-1} K^{-1}.

For getting additional explanations on the reaction course, an examination of the effect of the nature of the solvent was performed. Thus styrene was hydrogenated in the presence of **1a** in THF and CH_2Cl_2. The olefin was completely converted to ethylbenzene with longer reaction times than in MeOH in the order MeOH < THF < CH_2Cl_2. In addition a reaction carried out in MeOD ensured that no hydrogen arising from the solvent was incorporated in ethylbenzene. On the basis of a statistical treatment of the kinetic data two rate laws can express the reaction course. These results prompted us to depict the mechanisms shown in Scheme 3.



Scheme 3. Proposed mechanisms for the hydrogenation of styrene catalysed by **1a**.

The first stage of the catalytic cycle corresponds to a net heterolytic splitting of the molecular hydrogen, with protonation of the ligand and formation of palladium-(II) hydride **B** in equilibrium with **B′**. We think that in our case a net heterolytic hydrogen cleavage resulting via oxidative addition of H_2, followed by reductive elimination of HX (which may be base-assisted again), might not be likely owing to the unfavourable oxidative process from Pd(II) to Pd(IV). Successively, fast π-coordination of a styrene molecule occurs by rupture of the Pd–O or Pd–OAc coordinating bond giving **C**, followed by the semi-hydrogenation of the substrate, which leads to the formation of the alkyl intermediate **D**. At this point, two different pathways could be taken into account: (i) transfer of the second hydrogen atom from the ligand to the σ-coordinated substrate, with formation of ethylbenzene and restoration of complex **A**, but this route is in contrast with the result of the experiment carried out in MeOD; (ii) activation of a second hydrogen molecule with elimination of ethylbenzene and restoration of hydride intermediate **B**. In the latter case, complex **A** is the catalyst precursor. Two different rate determining steps (r.d.s.) can be inferred from pathway (ii): (I) the activation of the molecular hydrogen (formation of **B**); (II) the addition of hydrogen to intermediate **D**.

For (I), we only considered the two elementary steps

$$\mathbf{A} \underset{K_1}{\overset{H_2}{\rightleftharpoons}} \mathbf{B} \xrightarrow[k_3]{\text{styrene}} \mathbf{A} + \text{ethylbenzene} \tag{6}$$

assuming fast the subsequent steps. From the approximation of the transition state (6), it is possible to write that

$$d[\mathbf{B}]/dt \approx 0 = k_1[\mathbf{A}][H_2] - k_{-1}[\mathbf{B}] - k_3[\mathbf{B}][\text{styrene}] \tag{7}$$

being $K_1 = k_1/k_{-1}$. It easily follows that

$$[\mathbf{B}] = \frac{k_1[\mathbf{A}][H_2]}{k_{-1} + k_3[\text{styrene}]} \tag{8}$$

The partition of the overall initial concentration of the catalyst $[\mathbf{A}]_0$ can be expressed as

$$[\mathbf{A}]_0 = [\mathbf{A}] + [\mathbf{B}] = [\mathbf{A}]\left(1 + \frac{k_1[H_2]}{k_{-1} + k_3[\text{styrene}]}\right) \tag{9}$$

and then

$$r = \frac{k_3 K_1[\mathbf{A}]_0[H_2][\text{styrene}]}{1 + \frac{k_3}{k_{-1}}[\text{styrene}] + K_1[H_2]} \tag{10}$$

The individual equilibrium and rate constants K_1, k_{-1} and k_3 were calculated as $K_1 = 0.07$ mol^{-1} l, $k_{-1} = 2.22 \times 10^2$ s^{-1}, $k_3 = 3.17 \times 10^4$ mol^{-1} l s^{-1}.

For (II) the formation of intermediate **C** was not taken into account since it was assumed fast. The rate of hydrogenation is given by

$$r = -\mathrm{d}[\text{styrene}]/\mathrm{d}t = \mathrm{d}[\text{ethylbenzene}]/\mathrm{d}t = k_4[\mathbf{D}][\mathrm{H_2}] \quad (11)$$

In this case, the partition of the overall initial concentration of the catalyst $[\mathbf{A}]_0$ can be expressed as

$$[\mathbf{A}]_0 = [\mathbf{A}] + [\mathbf{B}] + [\mathbf{D}] \quad (12)$$

and it readily follows that

$$[\mathbf{B}] = K_1[\mathbf{A}][\mathrm{H_2}] \quad (13)$$

$$[\mathbf{D}] = K_2[\mathbf{B}][\text{styrene}] \quad (14)$$

$$[\mathbf{A}] = [\mathbf{A}]_0 + (1 + K_1[\mathrm{H_2}] + K_1K_2[\mathrm{H_2}][\text{styrene}]) \quad (15)$$

and then

$$r = \frac{K_1K_2k_4[\mathbf{A}][\mathrm{H_2}]^2[\text{styrene}]}{1 + K_1[\mathrm{H_2}] + K_1K_2[\mathrm{H_2}][\text{styrene}]} \quad (16)$$

Now the individual equilibrium and rate constants K_1, K_2 and k_4 were calculated as $K_1 = 1.08$ mol^{-1} l, $K_2 = 3.70 \times 10^4$ mol^{-1} l, $k_4 = 15.63$ mol^{-1} l s^{-1}.

The employed statistic program furnished strictly similar calculated SSQ and percentage errors on [styrene] and [ethylbenzene], as shown in Table 8, which do not allow a definitive choice between the two different r.d.s.

However, we think some elements are in favour of (I). The negative activation entropy ($\Delta S^{\neq} = -17.56 \pm 0.03$ cal mol^{-1} K^{-1}) is in accord with an order increase in the r.d.s., and the addition of hydrogen to complex **A** could be a good candidate to the role of r.d.s. On the contrary (II) does not consider any order increase. In addition, with the exception of the hydrogenation catalysed by **1a**, a variable induction period was always observed. This rises in the order **3a** ≈ **4a** < **2a** ≪ **5a**. The highest basicity of the ligand contained in complex **1a**, allows the fast formation of hydride intermediate **B** which, even being present in low concentration, is reactive enough to prime the reaction. For the other complexes, a diverse time interval is required to form the hydride intermediate, in accord with a r.d.s. controlled by the ligand basicity.

The low values found for K_1 in both cases, point out that the first equilibrium in Scheme 3 is shifted on the left, so that the hydride concentration in solution, during the catalysis, is very low. In fact, carrying the hydrogenation out in a NMR tube, the conversion of styrene into ethylbenzene was only observed, without noting any signal attributable to a hydride palladium(II) complex, even at −10°C.

Table 8
Calculated SSQ and % errors on [styrene] and [ethylbenzene] for the proposed r.d.s.

	SSQ	% error on [styrene]	% error on [ethylbenzene]
(I)	3.33	4.42	16.17
(II)	3.22	4.28	15.70

The presence of cationic intermediate **C** is well demonstrated by the slowing down of the reaction observed in the presence of an excess of acetate anion, after addition of sodium acetate (Pd:acetate = 1:3). This excess causes, on average, a halving of the ethylbenzene amount found in solution at the end of the reaction.

Finally, the values of E_a and $\Delta H^{\neq}$ ($E_a = 10.05 \pm 0.01$ kcal mol^{-1}, $\Delta H^{\neq} = 9.34 \pm 0.01$ kcal mol^{-1}) are higher than those of a diffusion controlled reaction (e.g. 2–4 kcal mol^{-1}) and in accord with an homogeneous process [26].

The unexpected higher reactivity found for **4a** compared to that of **2a**, can be explained by considering that the R group may not only influence the ligand basicity but even weakening the Pd-(carbonylic oxygen of the ligand) coordinating bond. In fact, looking at Scheme 3, intermediate **B** can be thought in equilibrium with the cationic form **B′** where the neutral ligand is coordinated in a tridentate mode. The presence of such a Pd–O bond can be seen as a further obstacle to the coordination of the olefin to the metal. In the presence of a bromine atom, like in **4a**, this obstacle can be, at least partially, removed by the electron withdrawing effect of the halogen, which makes the carbonylic oxygen of the ligand less coordinating. On the other hand, in the presence of the strong electron withdrawing group NO_2, like in **5a**, the loss of basicity strongly retards the hydride formation and then the entire process. Some points deserving of attention derive from Table 7, where the results obtained with the other substrates are collected. In the hydrogenation of diphenylacetylene, at the end of the reaction, besides the saturated product, a little amount of *trans*-stilbene was present in solution. We think that this comes from a partial isomerisation of *cis*-stilbene which usually is the kinetic product for monohydride intermediate [16a]. The latter is quickly hydrogenated to 1,2-diphenylethane according to the fact that we did not detect its presence by gas-chromatographic analysis during the reaction. Such a partial isomerisation is also present in the hydrogenation of 1-octene and this is an additional proof for the formation of a monohydride species. The bulkiness of *trans*-stilbene, cyclooctene as well as *trans* and *cis* octene, prevents their complete hydrogenation.

4. Conclusions

A correlation between the basicity of some tridentate hydrazonic ligands and the catalytic activity of the

corresponding acetate palladium(II) complexes in the homogeneous hydrogenation of unsaturated C–C bonds has been found. This suggests a heterolytic activation of the molecular hydrogen, with protonation of the ligand and formation of a palladium(II) hydride complex. Kinetic studies on the hydrogenation of styrene catalysed by **1a**, have led us to suggest a possible mechanism of reaction (Scheme 3). Two stages can accomplish the task of r.d.s.: (I) is the addition of the molecular hydrogen to the starting complex **A**, with formation of the hydride intermediate **B**. (II) is instead the addition of hydrogen to the alkyl intermediate **D** with elimination of ethylbenzene. The found negative activation entropy and the presence of an induction time correlated with the ligand basicity are in favour of (I).

Acknowledgements

This work was supported by M.U.R.S.T (Ministero della Universita e della Ricerca Scientifica e Tecnologica). A particular thank is due to Dr C. Vignali for the ^{31}P-NMR spectra recording and the helpful suggestions.

References

[1] (a) G.P.C.M. Dekker, C.J. Elsevier, K. Vrieze, P.W.N.M. van Leeuwen, Organometallics, 11 (1992) 1598. (b) G.P.C.M. Dekker, C.J. Elsevier, K. Vrieze, P.W.N.M. van Leeuwen, C.F. Roobeek, J. Organomet. Chem. 430 (1992) 357. (c) G.K. Anderson, G.J. Lumetta, Organometallics, 4 (1985) 1542. (d) A.J. Paviglianiti, D.J. Minn, W.C. Fultz, J.L. Burmeister, Inorg. Chim. Acta 159 (1989) 65. (e) R.E. Rülke, J.G.P. Delis, A.M. Groot, C.J. Elsevier, P.W.N.M. van Leuween, K. Vrieze, K. Goubitz, H. Schenk, J. Organomet. Chem. 508 (1996) 109. (f) R.E. Rülke, D. Kliphuis, C.J. Elsevier, J. Fraanje, K. Goubitz, P.W.N.M. van Leuween, K. Vrieze, J. Chem. Soc. Chem. Commun. (1994) 1817. (g) B.A. Markies, D. Kruis, M.H.P. Rietveld, K.A.N. Verkerk, J. Boersma, H. Kooijman, M.T. Lakin, A. Spek, G. van Koten, J. Am. Chem. Soc. 117 (1995) 5263. (h) J.G.P. Delis, M. Rep, R.E. Rülke, P.W.N.M. van Leuween, K. Vrieze, J. Fraanje, K. Goubitz, Inorg. Chim. Acta 250 (1996) 87. (i) V.G. Albano, C. Castellari, Organometallics 9 (1990) 1269. (l) F.P. Fanizzi, M. Lanfranchi, G. Natile, A. Tiripicchio, Inorg. Chem. 33 (1994) 3331. (m) V.G. Albano, F. Demartin, A. De Renzi, G. Morelli, A. Saporito, Inorg. Chem. 24 (1985) 2032. (n) A. De Renzi, G. Morelli, A. Panunzi, A. Vitagliano, Gazz. Chim. Ital. 117 (1987) 445. (o) G.W. Bushnell, K.R. Dixon, M.A. Khan, Can. J. Chem. 52 (1974) 1367.

[2] (a) B.R. James, Homogeneous Hydrogenation, Wiley-Interscience, New York, 1973. (b) G.W. Parshall, S.D. Ittel, Homogeneous Catalysis, Wiley-Interscience, New York, 1992. (c) H. Teunissen, C.J. Elsevier, J. Chem. Soc. Chem. Commun. (1997) 667. (d) A. Harthun, R. Giernoth, C.J. Elsevier, J. Bargon, J. Chem. Soc. Chem. Commun. (1996) 2483. (e) E.W. Stern, P.K. Maples, J. Catal. 27 (1972) 120. (f) In Sik Cho, H. Alper, Tetrahedron Lett. 32 (1995) 5673. (g) R. van Asselt, C.J. Elsevier, J. Mol. Catal. 65 (1991) L13.

[3] (a) D.H. Doughty, M.F. McGuiggan, H.H. Wang, L.H. Pignolet, in: M. Tutsui (Ed.), Fundamental Research in Homogeneous Catalysis, vol. 3, Plenum, New York, 1979, pp. 909. (b) D.H. Doughty, M.P. Anderson, A.L. Casalnuovo, M.F. McGuiggan, C.C. Tso, H.H. Wang, L.H. Pignolet, Catalytic aspects of metal phosphine complexes, in: E.C. Alyea, D.W. Meek (Eds.), Advances in Chemistry 196, American Chemical Society, Washington DC, 1982, pp. 65. (c) L.H. Pignolet, D.H. Doughty, in: L.H. Pignolet (Ed.), Homogeneous Catalysis with Metal Phosphine Complexes, Plenum, New York, 1983.

[4] (a) C.A. Ghilardi, S. Midollini, S. Moneti, A. Orlandini, G. Scapacci, J. Chem. Soc. Dalton Trans. (1992) 3371. (b) H. Hoberg, A. Ballestreros, A. Sigan, J. Organomet. Chem. 403 (1991) C19. (c) K. Tani, M. Yabuta, S. Nakamura, T. Yamagata, J. Chem. Soc. Dalton Trans. (1993) 2781. (d) E. Linder, H. Rauleder, P. Wegner, Z. Naturforsch. Teil B 39 (1984) 1224. (e) M.P. Anderson, A.L. Casalnuovo, B.J. Johnson, B.M. Mattson, A.M. Mueting, L.H. Pignolet, Inorg. Chem. 27 (1988) 1649. (f) T. Tsuda, S. Morikawa, T. Saegusa, J. Chem. Soc. Chem. Commun. (1989) 9. (g) H. Hoberg, A. Ballestreros, A. Sigan, J. Organomet. Chem. 403 (1991) C19.

[5] J.V. Allen, J.F. Bower, J.M.J. Williams, Tetrahedron Lett. 10 (1994) 1895.

[6] K.E. Frankcombe, K.J. Cavell, B.F. Yates, R.B. Knott, Organometallics 16 (1997) 3199.

[7] A. Bader, E. Lindner, Coord. Chem. Rev. 108 (1991) 27.

[8] (a) L. Costella, A. Del Zotto, A. Mezzetti, E. Zangrando, P. Rigo, J. Chem. Soc. Dalton Trans. (1993) 3001. (b) T.B. Rauchfuss, D.M. Roundhill, J. Am. Chem. Soc. 96 (1974) 3098. (c) T.B. Rauchfuss, D.M. Roundhill, J. Organomet. Chem. 59 (1973) C30. (d) T.B. Rauchfuss, J.C. Jeffrey, Inorg. Chem. 18 (1979) 2658. (e) T.B. Rauchfuss, F.T. Paitino, D.M. Roundhill, Inorg. Chem. 14 (1975) 652. (f) H.D. Empsall, E.M. Hyde, D. Pawson, B.L. Shaw, J. Chem. Soc. Dalton Trans. (1997) 1292.

[9] (a) S.T. Liu, H.E. Wang, M.C. Cheng, S.M. Peng, J. Organomet. Chem. 376 (1989) 333. (b) S.T. Liu, G.J. Liu, Inorg. Chem. 29 (1990) 4576. (c) S.T. Liu, G.J. Liu, C.H. Yeeh, M.C. Cheng, S.M. Peng, J. Organomet. Chem. 387 (1990) 83. (d) S.T. Liu, C.L. Tsao, M.C. Cheng, S.M. Peng, Polyhedron 9 (1990) 2579. (e) H.E. Wang, M.C. Cheng, G.H. Lee, S.M. Peng, S.T. Liu, J. Organomet. Chem. 445 (1993) 171. (f) M. Alvarez, N. Lugan, R. Mathieu, J. Chem. Soc. Dalton Trans. (1995) 2755. (g) H. Yang, M. Alvarez, N. Lugan, R. Mathieu, J. Chem. Soc. Chem. Commun. (1995) 1721. (h) K.K. Hij, S.D. Perera, B.L. Shaw, J. Chem. Soc. Dalton Trans. (1994) 3589. (l) L. Ahmad, S.D. Perera, B.L. Shaw, M. Thornton-Pett, J. Chem. Soc. Dalton Trans. (1997) 2607.

[10] R.E. Rülke, V.E. Kaasjager, D. Kliphuis, C.J. Elsevier, P.W.N.M. van Leeuwen, K. Vrieze, K. Goubitz, Organometallics 15 (1996) 668.

[11] (a) Y. Kataoka, Y. Tsuij, O. Matsumoto, M. Ohashi, T. Yamagata, K. Tani, J. Chem. Soc. Chem. Commun. (1995) 2099. (b) G.J.P. Britovsek, K.J. Cavell, M.J. Green, F. Gerhards, B.W. Skelton, A.H. White, J. Organomet. Chem. 533 (1997) 201.

[12] (a) D.E. Barber, Z. Lu, T. Richardson, R.H. Crabtree, Inorg. Chem. 31 (1992) 4709. (b) A.H. Vetter, A. Berkessel, Synthesis (1995) 419.

[13] P. Pelagatti, Ph.D. Thesis, University of Parma, 1998.

[14] P. Pelagatti, A. Venturini, A. Leporati, M. Carcelli, M. Costa, A. Bacchi, G. Pelizzi, C. Pelizzi, J. Chem. Soc. Dalton Trans. (1998) 2715.

[15] (a) A. Bacchi, M. Carcelli, P. Pelagatti, C. Pelizzi, G. Pelizzi, Gazz. Chim. Ital. 124 (1994) 429. (b) A. Bacchi, M. Carcelli, M. Costa, A. Leporati, E. Leporati, P. Pelagatti, C. Pelizzi, G. Pelizzi, J. Organomet. Chem. 535 (1997) 107.

[16] (a) B.R. James, Comprehensive Organometallic Chemistry, vol. 8, 295 and references therein cited. (b) G. Henrici-Olivé, S. Olivé,

J. Mol. Catal. 1 (1975/76) 121. (c) F. Hutschka, A. Dedieu, J. Chem. Soc. Dalton Trans. (1997) 1899. (d) D. Sellmann, G.H. Rackelmann, F.W. Heinemann, Chem. Eur. J. 3 (1997) 2071.

[17] A. Altomare, M.C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A.G. Moliterni, G. Polidori, R. Spagna, SIR97, A new program for solving and refining crystal structures, Institute for the Research and Development of Crystallographic Methodologies, C.N.R., Bari, Italy.

[18] G. Sheldrick, SHELXL97, Program for Structure Refinement, University of Göttingen, Germany, 1997.

[19] M. Nardelli, J. Appl. Crystallogr. 28 (1995) 659.

[20] L. Zsolnai, H. Pritzkow, ZORTEP, ORTEP, original program modified for PC, University of Heidelberg, Germany.

[21] Q. Liu, F. Takemura, A. Yabe, J. Chem. Eng. Data 41 (1996) 1141.

[22] (a) R.H. Contreras, J.C. Facelli, in: G.A. Webb (Ed.), Annual Reports in NMR Spectroscopy, Academic, London, 1993. (b) C.J. Jameson, in: J.G. Verkade, L.D. Quin (Eds.), Phosphorous-31 NMR Spectroscopy in Stereochemical Analysis, VHC, Deerfield Beach, FL, 1987. (c) R.E. Rülke, V.E. Kaasjager, P. Wehman, C.J. Elsevier, P.W.N.M. van Leeuwen, K. Vrieze, J. Fraanje, K. Goubitz, A.L. Spek, Organometallics, 15 (1996) 3022.

[23] (a) A. Bacchi, M. Carcelli, M. Costa, P. Pelagatti, C. Pelizzi, G. Pelizzi, J. Chem. Soc. Dalton Trans. (1996) 4239. (b) N.F. Curtis, J. Chem. Soc. A (1968) 1569. (c) E. Kokot, G.M. Mokler, G.L. Sefton, Inorg. Chem. 13 (1974) 6. (d) F. Dawans, J. Dewailly, J. Organomet. Chem. 76 (1974) 53. (e) T.A. Stephenson, S.M. Morchouse, A.R. Powell, G. Wilkinson, J. Inorg. Nucl. Chem. (1965) 3632. (f) T.A. Stephenson, G. Wilkinson, J. Chem. Soc. 29 (1967) 2122.

[24] (a) G. Buzzi Ferraris, Analisi e Identificazione di Modelli, CLUP Milan, 1982.

[25] Eq. (1) has been embedded in the non linear regression subroutine BURENL, where the ODE integration has been performed through the subroutine LSODA. The least-square sum has been calculated on both styrene and ethylbenzene molar concentration as follows: $SSQ = \Sigma_{k=1}^{NP}\{[[STY]_k^{calc} - [STY]_k^{exp}]/[STY]_k^{exp}\}^2 + \Sigma_{k=1}^{NP}\{[[ETB]_k^{calc} - [ETB]_k^{exp}]/[ETB]_k^{exp}\}^2$. To discriminate the different models from a statistical point of view, only the SSQ and % average errors, as defined below, can be adopted. $\%STY = (1/NP)(\Sigma_{k=1}^{NP}\|[[STY]_k^{calc} - [STY]_k^{exp}]/[STY]_k^{exp}\|)$. $\%ETB = (1/NP)(\Sigma_{k=1}^{NP}\|[[ETB]_k^{calc} - [ETB]_k^{exp}]/[ETB]_k^{exp}\|)$. It was found that SSQ is 2.31, % error on [styrene] is 3.15, % error on [ethylbenzene] is 13.15. For references on subroutine BURENL see: (a) G. Buzzi Ferraris, Ing. Chim. Ital. 3 (1967) 101. (b) G. Buzzi Ferraris, Ing. Chim. Ital. 4 (1968) 171. For references on subroutine LSODA see (a) A.C. Hindmarsh, ACM Signum Newslett. 15 (1980) 10. (b) L.R. Petzold, Sandia Nat. Lab. Rep. (1980) 8230.

[26] (a) J.L. Lin, C.U. Pittman Jr., J. Organomet. Chem. 512 (1996) 69. (b) M. Bourdart, R.J. Madon, J.P. O'Connell, AlChE J. 24 (5) (1978) 904. (c) M. Bourdart, E.E. Gonzo Jr., J. Catal. 52 (1978) 462.