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Chemoselective homogeneous hydrogenation of phenylacetylene using thiosemicarbazone and thiobenzoylhydrazone palladium(II) complexes as catalysts

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A series of monometallic palladium(II) complexes with thiosemicarbazones and thiobenzoylhydrazones has been synthesized and characterised by spectroscopic methods. The crystal structures of chloro(phenyl 2-pyridyl ketone thiosemicarbazonato)palladium(II) **1a** and chloro(phenyl 2-pyridyl ketone thiobenzoylhydrazonato)palladium(II) **2** were also determined. The catalytic activity of the complexes in the homogeneous hydrogenation of phenylacetylene was tested with particular regard to the chemoselectivity from a triple to a double bond. Using chloro-complexes a high chemoselectivity was always observed. Results of a kinetic study of the hydrogenation of phenylacetylene in the presence of chloro(methyl 2-pyridyl ketone thiosemicarbazonato)palladium(II) **3** as catalyst provided suggestions for the elucidation of the catalytic cycle of the reaction.

In our recent studies on homogeneous hydrogenation of unsaturated substrates catalysed by palladium(II) complexes we reported that thiosemicarbazone complexes of formula [PdL(X)] [HL = 2-(diphenylphosphino)benzaldehyde thiosemicarbazone; X = CH_3CO_2, Cl or I] were not able to hydrogenate styrene and phenylacetylene under atmospheric pressure of hydrogen at 25 °C.[1] On the other hand, hydrazone complexes of formula [PdL′(X)] [HL′ = 2-(diphenylphosphino)benzaldehyde benzoyl-,[2] methylpyridyl-, nicotinoyl- or isonicotinoylhydrazone[1]] showed different catalytic activities towards styrene and phenylacetylene depending on the nature of the anionic ligand X and the groups present in the hydrazonic chain of the ligands. Fundamental was the presence, in the complexes, of a stabilising Pd–P bond in order to prevent their decomposition under a hydrogen atmosphere, as well as the presence of a labile co-ordinating bond prone to dissociate to provide an available co-ordination site. The determinant for the chemoselectivity of the process was the nature of the counter ion bonded to the palladium atom; thus when X was chloride a high chemoselectivity from a triple to a double bond was observed.

In order to find other palladium(II) complexes able to behave as catalysts for the selective hydrogenation of terminal alkynes to the corresponding alkenes and to get more detailed information on the influence of the nature of the donor atoms of the ligand, we designed new tridentate NNS ligands containing a donor atom with a high affinity for palladium(II) and another one forming a more labile co-ordination bond. We synthesized two thiosemicarbazone (HL^1 and HL^3) and two thiobenzoylhydrazone (HL^2 and HL^4) ligands and the respective palladium (II) complexes of formula [Pd(NNS)X]. These were tested as catalysts in the homogeneous hydrogenation of styrene and phenylacetylene. The presence of a soft donor atom, like sulfur, assures the stability of the complexes under a hydrogen atmosphere, while the breakage of the labile pyridine–palladium bond can allow the co-ordination of an additional molecule (molecular hydrogen or unsaturated substrate), in accord with the general concept of hemilability of ligands as introduced by Jeffrey and Rauchfuss.[3]

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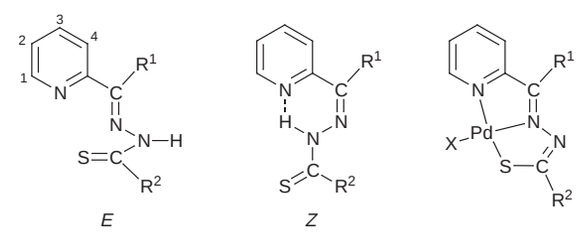
In the literature there are few examples concerning the catalytic applications of thiosemicarbazone or thiobenzoylhydrazone complexes,[4] this making more interesting and stimulating the study of their use as homogeneous catalysts. The crystal structures of chloro(phenyl 2-pyridyl ketone thiosemicarbazonato)palladium(II) **1a** and chloro(phenyl2-pyridyl ketone thiobenzoylhydrazonato)palladium(II) **2** are also reported.



R^1 = Ph, R^2 = NH_2 (HL^1)
R^1 = Ph, R^2 = Ph (HL^2)
R^1 = CH_3, R^2 = NH_2 (HL^3)
R^1 = CH_3, R^2 = Ph (HL^4)

X = Cl **1a**, CH_3CO_2 **1b**, I **1c**
X = Cl **2**
X = Cl **3**
X = Cl **4**

Results and Discussion

Synthesis

Ligands HL^1 and HL^2 were synthesized following literature methods.[5,6] The structures of all compounds were confirmed by elemental analyses, IR and ^{1}H NMR spectroscopies. In the IR spectrum of the ligands the absence of any bands in the region 2600–2500 cm^{-1}, due to ν(SH), indicates the absence of thiolic forms, supporting the presence of HL^1–HL^4 in the thioketo form.[5,6] Compounds containing the C=N moiety can exist in the *E* or *Z* form or as a mixture of *E*/*Z* isomers. By ^{1}H NMR spectroscopy, on the basis of data previously reported in several works concerning N-heteroaromatic thiosemicarbazones, it was possible to assign the correct conformation to the different products.[6] The most sensitive signal is that belonging to the NH group, *i.e.* δ(NH) 14–15 for the *Z* form and 9–12 for the *E* form. Thus, the *Z* conformation was assigned to compounds HL^1 and HL^2 for which δ(NH) 13.80 and 13.59 respectively. For the

Table 1 Selected IR and ^{1}H NMR [$CDCl_3$ for HL^1–HL^4, **1a** and **1c**; $(CD_3)_2SO$ for **1b**, **2**, **3** and **4**] data for ligands and complexes

	IR/cm^{-1} [a]						δ_H [b]				
Compound	ν(N–H)	ν(C=N)	Thioamide II	Thioamide III	ν(NCS)	ν(CS)	N–H	H^1	H^2	H^3	H^4
HL^1	3131m	1595vs [c]	1499m	1469vs	1422vs	972w	13.80s	8.81 (dd)	7.39 (td)	7.77 (td)	7.30 (dd)
HL^2	3301w	1585m	1478vs	1447s	1420s	969s	13.59s	8.57 (d)	*d*	7.78 (td)	7.91 (d)
(*E*)							8.89s	8.61 (br d)	7.29 (t)	7.70 (t)	7.95 (d)
HL^3	3155w	1602vs [c]	1500vs	1465vs	1430vs	987w					
(*Z*)							12.46s	8.74 (dd)	7.37 (td)	7.86 (td)	7.54 (d)
HL^4	3283m	1590s	1465s	1432ms	1405s	979w	9.51 (br) s	8.57 (d)	7.22 (br t)	7.73 (m)	7.73 (m)
1a	—	1625s [c]	1497s	1451vs	1437s	955vw	—	8.89 (d)	7.52 (t)	7.78 (t)	7.08 (d)
1b	—	1588s [c]	1567s	1450m	1428s	939vw	—	8.70 (d)	7.50 (t)	7.92 (t)	6.38 (d)
1c	—	1627vs [c]	1491m	1452vs	1442vs	954vw	—	9.06 (dd)	*d*	7.99 (td)	6.99 (d)
2	—	1594w	1499m	1457vs	1432s	963w	—	8.73 (d)	7.53 (t)	8.15 (td)	*d*
3	—	1598s [c]	1502s	1455vs	1441s	1002vw	—	8.53 (d)	7.61 (t)	8.14 (t)	*e*
4	—	1598w	1488m	1464s	1437ms	1002vw	—	8.64 (d)	7.59 (t)	8.27 (t)	8.11 (d)

[a] ν(NH_2): L^1, 3409m, 3228m; L^3, 3420m, 3365m; **1a**, 3445m, 3277m–3126m; **1b**, 3462m, 3277m–3142m; **1c**, 3448m, 3277m–3107m; **3**, 3415m, 3313s. [b] In order to save space coupling constants are not reported. δ(NH_2): L^1, 6.48 (2 H, s); L^3, 7.26 (1 H, s), 6.39 (1 H, s); **1a**, 5.32 (2 H, s); **1b**, 5.07 (2 H, s); **1c**, 7.91 (2 H, s); **3**, 7.79 (3 H, m). [c] Contribution due to δ(NH_2). [d] Overlapping with the signals of the Ph groups. [e] Overlapping with the signal of the NH_2 group.

ligands containing the 2-acetylpyridine substructure the NH signal is much more shielded (δ 8.89 for HL^3 and 9.51 for HL^4) and the *E* conformation was assigned. A partial conversion from the *E* into the *Z* form was observed for HL^3 in $CDCl_3$ solution after 24 h (*E*:*Z* = 60:40) (Table 1).

Chloro-, iodo- and acetato-palladium(II) complexes were obtained by reaction between $Li_2[PdCl_4]$, $K_2[PdI_4]$ or $Pd(CH_3CO_2)_2$ and HL^1–HL^4 at room temperature in a 1:1 molar ratio. Complexes **1a–1c** and **2–4** are air stable for a long time both in solution and the solid state. In all the palladium(II) complexes the thiohydrazones behave as tridentate NNS ligands, co-ordinating through the pyridinic nitrogen, the iminic nitrogen and the sulfur atom giving rise to an essential square-planar structure, involving two five-membered rings. The deprotonation of the ligands, in complexes **1–4**, is clearly indicated both by the absence of ν(NH) in the IR spectrum (Table 1) [5,7] and the absence, in the ^{1}H NMR spectrum, of the singlet belonging to the same group (Table 1).[5,8] Moreover, the shift of ν(C=N) together with the intensity lowering of ν(C=S) in the IR spectrum, indicate Pd–N_{imine} and Pd–S co-ordination.[9,10] In complex **1b** the presence of the acetato group is confirmed, by the presence of a singlet at δ 2.30 in the ^{1}H NMR spectrum, and two bands in the IR spectrum at 1614 and 1287 cm^{-1} belonging to asymmetric and symmetric stretching of the carboxylate group respectively, having the characteristic values for monodentate co-ordination of this anion.[7,9]

Crystal structures

Figs. 1 and 2 show perspective views of the molecular structures of complexes **1a** and **2**, respectively, along with the labelling scheme. Table 2 summarises the most relevant geometric parameters for the two molecules. In both structures the monodeprotonated ligand co-ordinates the palladium by means of the three donor atoms N1, N2 and S, and a chloride anion, *trans* to N2, completes the planar square co-ordination of the metal and satisfies the electroneutrality of the complex. As a result of metal chelation, two adjacent five-membered rings are formed upon co-ordination.

Table 2 shows that there are no statistically significant differences in the geometry of the chelating rings between the two complexes. In both cases the metal and the four donor atoms are coplanar within 0.04 Å, and the square is distorted in the plane by the strains due to chelation. The largest deviation from ideality (about 14°) is in the angle S–Pd–N1. The molecular backbone C7–C13, N1–N3, S is planar, within 0.15 Å in both cases. The phenyl group C1–C6 makes a dihedral angle with the molecular backbone of 72° for **1a** and 54° for **2**. In the latter the phenyl C14–C19 makes a dihedral angle of 11° with the molecular backbone. In **1a** the terminal NH_2 group is planar, indicating sp^2 hybridisation for N4. The bond order along the two chelation rings can be examined by comparing the geometry of the present compounds with those of two closely related copper(II) complexes of similar ligands, differing only in the nature of the group substituted at N4, $\overline{N(CH_2)_5CH_2}$ and propyl, respectively.[10] In the former the ligand is deprotonated, as in the present work, in the latter the ligand is neutral. The most relevant differences are localised on the chelation ring containing S, C13, N3 and N2. In the N-propyl copper complex with the neutral ligand the double bond character is concentrated on the C–S bond (1.698 Å), while C–N and N–N have similar lengths (1.366 and 1.357 Å respectively). The deprotonation of the ligand in the $\overline{N(CH_2)_5CH_2}$ copper complex shifts the double-bond character to the C–N bond, which shortens to 1.335 Å while the C–S bond elongates to 1.750 Å. The N–N bond does not change (1.358 Å). In the two palladium complexes the double-bond character of the C–N bond is strengthened [C–N 1.321(5), 1.31(1) Å], while the N–N bonds are somewhat weakened [1.380(4), 1.37(1) Å]. The C–S bonds [1.745(4), 1.74(1) Å] have strengths similar to those of the deprotonated copper complex. The significant elongation of the N2–N3 bond in the palladium complexes is probably

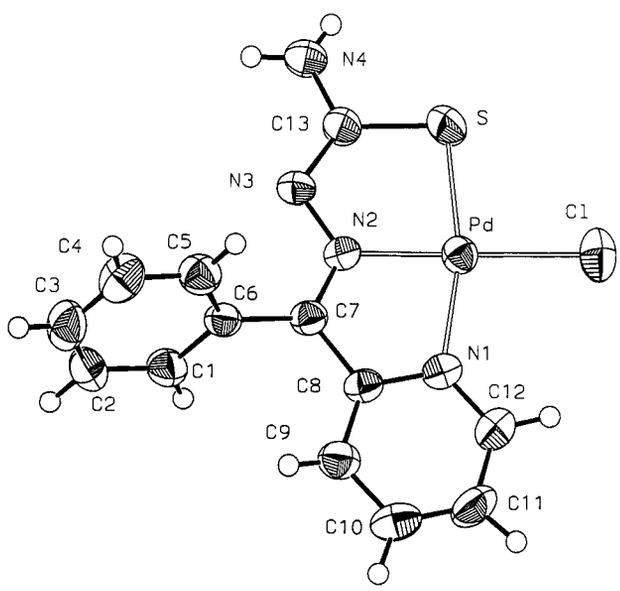


Fig. 1 Perspective view and labelling scheme of compound **1a**, with anisotropic displacement parameters drawn at 50% probability level

Table 2 Selected bond distances (Å) and angles (°) for complexes **1a** and **2**

	1a	**2**
Pd–N2	1.962(3)	1.94(1)
Pd–N1	2.041(3)	2.06(1)
Pd–S	2.241(1)	2.245(4)
Pd–Cl	2.304(1)	2.287(4)
S–C13	1.745(4)	1.74(1)
N1–C8	1.359(5)	1.40(2)
N2–C7	1.310(5)	1.35(2)
N2–N3	1.380(4)	1.37(1)
N3–C13	1.321(5)	1.31(1)
C7–C8	1.471(5)	1.45(2)
N4–C13	1.334(5)	
N2–Pd–N1	81.1(1)	82.3(5)
N2–Pd–S	84.8(1)	84.3(4)
N1–Pd–S	165.8(1)	166.5(3)
N2–Pd–Cl	177.0(1)	179.5(3)
N1–Pd–Cl	98.6(1)	97.3(4)
S–Pd–Cl	95.52(5)	96.1(2)
C13–S–Pd	95.2(1)	95.4(5)
C8–N1–Pd	111.9(2)	108.9(9)
C7–N2–Pd	116.3(3)	117.7(9)
N3–N2–Pd	122.9(2)	123.8(9)
C13–N3–N2	111.6(3)	112(1)
N2–C7–C8	115.1(3)	113(1)
N1–C8–C7	115.0(3)	118(1)
N3–C13–S	125.2(3)	124(1)

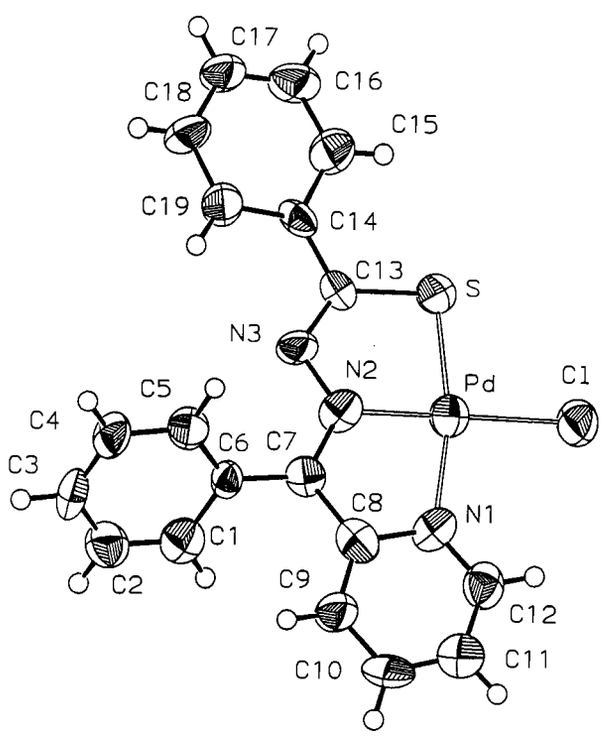


Fig. 2 Perspective view and labelling scheme of compound **2**; details as in Fig. 1

due to the nature of the metal, as suggested by the similar elongation observed for the C7–N2 bonds [1.310(5) and 1.35(2) Å for **1a** and **2** compared to 1.293 and 1.294 Å for the copper complexes]. As regards the co-ordination sphere of the palladium, a search of the Cambridge Crystallographic Database revealed that there are only seven other crystalline structures containing a palladium co-ordinated to two nitrogens, one sulfur and one chlorine, with the latter *trans* to one nitrogen. The Pd–N2 distances found in **1a** and **2** are among the shortest observed for these systems, which have a mean value of 2.01(1) Å. The co-ordination geometry of palladium in **1a** and **2** agrees well only with the one observed for chloro(3-thiosemicarbazonebutan-2-one oximate-*S*,*N*,*N*′)palladium(II)[11] [Pd–Cl 2.301(3), Pd–N2 1.954(5), Pd–N1 2.006(5), Pd–S 2.247(4) Å].

Table 3 Hydrogenation data for phenylacetylene using complexes **1a–1c** as catalysts at 30 °C and 1 atm of hydrogen in methanol for 24 h. [cat] = 1.44×10^{-3}, [phenylacetylene] = 1.44×10^{-1} mol dm^{-3}

Entry	Complex	Phenylacetylene (%)	Styrene (%)	Ethylbenzene (%)
1	**1a**	—	92	8
2	**1b**	—	44	56
3	**1c**	100	—	—

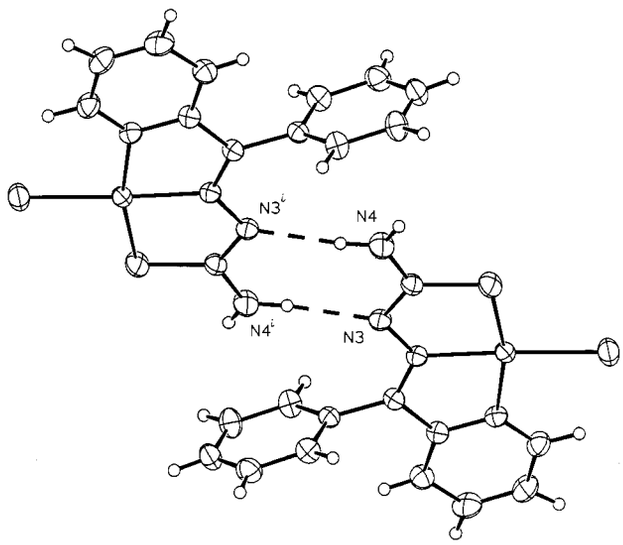


Fig. 3 Hydrogen-bonded dimeric unit characterising the crystal packing of compound **1a**

The crystal packing of complex **1a** is characterised by dimeric units based on the hydrogen bond N4 · · · N3^{i} 3.00(1) Å, N4–H · · · N3^{i} 174(5)° (i $1 - x$, $-y$, $1 - z$), as shown in Fig. 3. The packing of **2** is mainly based on van der Waals interactions.

Catalysis

All the complexes were tested as catalysts in the homogeneous hydrogenation of styrene and phenylacetylene at 30 °C and at atmospheric pressure of hydrogen for 24 h, using dmf, pyridine or methanol as solvent. Complexes **1a**, **1b** and **1c** showed very different catalytic behaviour in methanol (Table 3). Whereas iodo-complex **1c** was not able to hydrogenate phenylacetylene at all (Table 3, entry 3), acetato-complex **1b** showed a good catalytic activity with a low chemoselectivity, as shown in entry 2. At the end of the reaction it was not possible to recover the starting complex owing to the probable formation of a phenylethynylpalladium(II) complex, the instability of which prevented its characterisation.[1,2]

In contrast to the acetato- and iodo-complexes, chloro-complex **1a** was able to hydrogenate completely phenylacetylene with a good chemoselectivity (Table 3, entry 1). Using **1a** as catalyst the same catalytic behaviour was observed for the hydrogenation of oct-1-yne which was completely converted into oct-1-ene in 24 h. The hydrogenation of pure styrene took place only in the presence of **1b**, leading to the formation of ethylbenzene and partial decomposition of the complex in 48 h of reaction.

Since the chemoselectivity of the hydrogenation reaction is an important aspect of this process,[12] we concentrated our attention on the catalytic behaviour of the chloro-complexes which were tested as catalysts in the homogeneous hydrogenation of phenylacetylene at 30 °C and at atmospheric pressure of hydrogen, using dmf or pyridine as solvent for 24 h (chloride complexes **2–4** are scarcely soluble in methanol). In Table 4 are

Table 4 Hydrogenation data for phenylacetylene using complexes **1–4** as catalysts at 30 °C and 1 atm of hydrogen for 24 h. [cat] = 1.44×10^{-3}, [phenylacetylene] = 1.44×10^{-1} mol dm^{-3}

Entry	Complex	Solvent	Phenylacetylene (%)	Styrene (%)	Ethylbenzene (%)
1	**1a**	dmf	61	37	2
2	**2**	dmf	1	96	3
3	**3**	dmf	—	95	5
4*	**3**	dmf	—	85	15
5	**4**	dmf	2	94	4
6	**1a**	Pyridine	70	30	—
7	**2**	Pyridine	77	22	1
8	**3**	Pyridine	75	23	2
9	**4**	Pyridine	71	28	1

* In the presence of KPF_6 in a molar ratio Pd : K = 1 : 5; after 36 h the percentage of ethylbenzene was 51%.

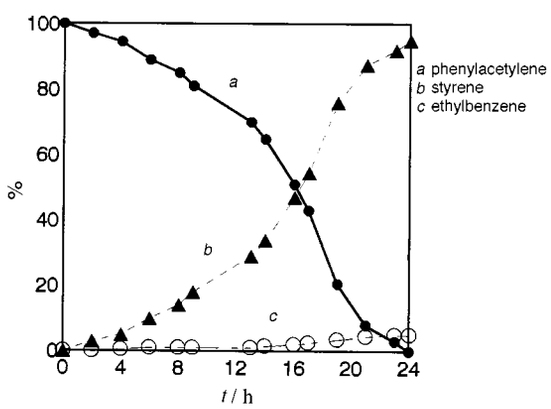


Fig. 4 Hydrogenation of phenylacetylene in the presence of complex **3**. Reactions conditions: [Pd] = 1.440×10^{-3}; [phenylacetylene] = 1.440×10^{-1} mol dm^{-3}; solvent dmf; H_2 pressure = 1 atm (101 325 Pa); T = 30 °C

listed the percentages of styrene and ethylbenzene found for the different hydrogenation tests.

In all cases a good chemoselectivity from the triple to double bond was observed and, in support, no catalytic activity was observed using pure styrene as substrate, even for reaction times longer than 24 h (the longest being 36 h). With dmf as solvent the conversion of phenylacetylene was always practically complete except for **1a** (Table 4, entry 1), but this fact is ascribable to its low solubility in this solvent. In pyridine the conversions were lower than in dmf but still a good chemoselectivity was observed (Table 4, entries 6–9).

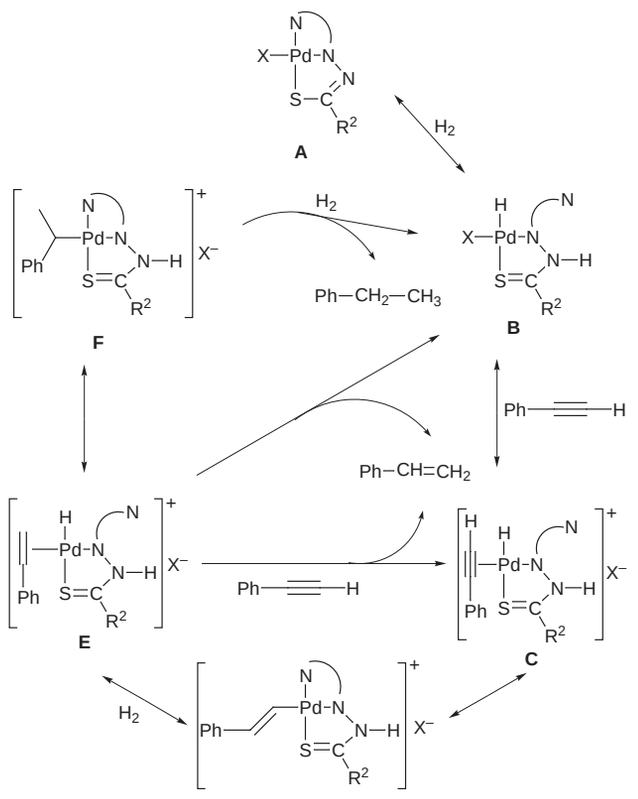
The chloro-complexes used as catalysts were always recovered unchanged and the amount of black palladium present in solution at the end of the process was insignificant. A small amount of ethylbenzene was found in the hydrogenation reaction of phenylacetylene, but even when the latter was completely converted into styrene we did not observe further formation of ethylbenzene, rather a slow decomposition of the catalysts with formation of black palladium.

The nature of the groups present in the ligands (R^1 = Ph or CH_3, R^2 = NH_2 or Ph) did not play any specific role towards the catalytic behaviour of the complexes but was determinant for their solubility. Thus **1a**, which is the least soluble complex in dmf, showed the worst catalytic activity. Complex **3** was chosen to perform a more detailed kinetic study. Fig. 4 shows the profile of the percentage conversion of phenylacetylene and the percentage yields of styrene and ethylbenzene with time, in a typical experiment, using **3** as catalyst dissolved in dmf.

The presence of an induction time was eliminated by carrying out the hydrogenation tests at 50 °C. By using complex **3** and varying one at a time the concentration of the components

Table 5 Kinetic data for the hydrogenation of phenylacetylene to styrene catalysed by **3** in dmf at 50 °C

10^3[**3**]/ mol dm^{-3}	[PhC≡CH]/ mol dm^{-3}	$10^3[H_2]$/ mol dm^{-3}	$p(H_2)$/ atm	$10^{-7}r$/ mol dm^{-3} s^{-1}
1.428	0.146	2.379	1	2.46 ± 0.30
1.428	0.218	2.379	1	3.50 ± 0.35
1.428	0.302	2.379	1	5.58 ± 0.52
1.428	0.443	2.379	1	8.29 ± 0.58
1.071	0.146	2.379	1	1.32 ± 0.11
2.143	0.146	2.379	1	3.07 ± 0.52
2.857	0.146	2.379	1	3.89 ± 0.25
1.428	0.146	0.595	0.25	0.63 ± 0.09
1.428	0.146	1.190	0.50	1.12 ± 0.10
1.428	0.146	1.785	0.75	1.54 ± 0.15



Scheme 1 Postulated mechanism for the hydrogenation of phenylacetylene

of the reaction mixture at 50 °C the reaction rates summarised in Table 5 were obtained. A plot of log r *versus* log [phenylacetylene] yielded a straight line of slope 0.96, indicating that the reaction is approximately first order in [phenylacetylene]. In the same way it is possible to obtain the reaction orders for [**3**] (1.09 ≈ 1) and [H_2] (0.94 ≈ 1). From these data the rate law can be represented by equation (1). By taking the kinetic results and

$$r = -\mathrm{d}[\mathrm{PhC{\equiv}CH}]/\mathrm{d}t = k[\mathrm{PhC{\equiv}CH}][\mathbf{3}][H_2] \qquad (1)$$

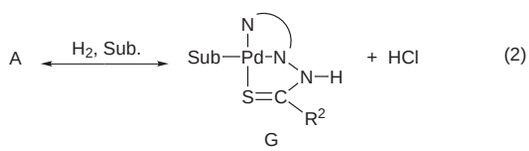
the activity data into account, a catalytic cycle for the selective hydrogenation of phenylacetylene to styrene shown in Scheme 1 can be advanced.

The interaction of hydrogen with complex **A** is likely the first stage of the reaction. The presence of basic sites in the ligand (hydrazone nitrogen being more basic than the pyridine one[5]) favours an heterolytic activation of molecular hydrogen[13] with protonation of the ligand and formation of a palladium hydride complex,[14] where the pyridine ring may be displaced from the co-ordination plane (**B** in Scheme 1). The nature of the

counter ion X bonded to palladium apparently plays a predominant role in driving the chemoselectivity of the process. So when X is a good leaving group like acetate both phenylacetylene and styrene can π co-ordinate to the metal centre and intermediate **C** can be formed smoothly by both unsaturated C–C bonds. Instead when X is an iodine atom its high affinity to palladium prevented the formation of **C** blocking the reaction at the stage of the intermediate **B**. A good compromise is reached with X = Cl because only phenylacetylene and not styrene is able to displace a chlorine atom from the co-ordination plane, resulting in the observed chemoselectivity. On the other hand this would not be explained by considering the possibility that the pyridine group is exclusively removed by phenylacetylene after activation of the molecular hydrogen; in this case the nature of the X group should not play any important role, taking immediately a position outside the co-ordination sphere of the palladium, and the fact that only the acetate complex can hydrogenate the olefinic substrate could not be explained.

Moreover the role played by the counter ion on the chemoselectivity of the process is confirmed by the fact that on conducting the hydrogenation of phenylacetylene in the presence of KPF_6 as ion-exchange agent and using **3** as catalyst in dmf an increasing amount of ethylbenzene was found after 24 h of reaction (Table 4, entry 4). The non-co-ordinating anion PF_6^- makes easier the formation of a cationic intermediate, allowing the co-ordination of styrene which is, then, hydrogenated.

The data concerning the chemoselectivity and its observed decrease in the presence of KPF_6 induce us to exclude the possibility of having a palladium(0) intermediate species which could be hypothesised according to equation (2). If this



Sub. = Phenylacetylene or styrene

equation were valid both phenylacetylene and styrene could co-ordinate to the metal centre and be hydrogenated by subsequent oxidative addition of hydrogen on the palladium(0) complex **G**. The cationic intermediate **C** in Scheme 1 can be confirmed by the slowing down of the reaction when an excess of chloride ion is present in solution by addition of $NBu^n_4Cl^-$ ($Pd:Cl^-$ molar ratio = 1:3). This excess causes, on average, a halving of the amount of styrene present in solution after 24 h of reaction.

The displacement of a pyridine from the co-ordination plane had been hypothesised by us,[1] but also in the literature there are some examples where the pyridine nitrogen is replaced by other ligands like CO,[15] chloride,[16] allenes,[17] phosphines[18] and even olefins in the presence of bulky pyridine systems.[19] The breaking of the $Pd–N_{py}$ bond can be favoured by the *trans* effect of the sulfur atom which occupies a *trans* position with regard to the pyridine ring.

After π co-ordination of phenylacetylene to palladium, the hydride is transferred to the co-ordinated substrate forming an alkenyl complex **D**. At this stage of the catalytic cycle a molecule of hydrogen can be activated leading to palladium hydride complex **E** with π co-ordinated styrene. Chloride anion or a molecule of phenylacetylene readily displaces styrene leading to intermediate **B** or **C** respectively, which can start the catalytic cycle again. Nevertheless, if the hydride in complex **E** is transferred to π-co-ordinated styrene, alkyl complex **F** is formed which, by activation of an additional molecule of hydrogen, can restore the intermediate **B** with elimination of ethylbenzene. Thus the formation of ethylbenzene depends on the relative rates of displacement of styrene by X or phenylacetylene (from **E** to **B** or from **E** to **C**) and by the migration of the hydride from palladium to π-co-ordinated styrene (from **E** to **F**). The latter is expected to be favoured when $X = CH_3CO_2$ in accord with the experimental results. When all substrate is consumed, intermediate **B** is reconverted into **A** in the absence of hydrogen. The proposed mechanism seems to be in accord with the experimentally found orders of the reactants. The rate-determining step could be the addition of hydrogen to the intermediate **D** formed by interaction of the complex **B** and phenylacetylene. The role played by the solvent is not only to dissolve the complex to give an homogeneous solution, but seems to involve other factors. Its basicity does not seem important in making easier the heterolytic cleavage of the molecular hydrogen;[20] in fact the good catalytic activity observed for **1a** and **1b** in a non-basic solvent like MeOH (Table 3, entries 1 and 2) and the lower catalytic activities found for all the complexes in the more basic solvent pyridine [$K_{b,py} = 2.3 \times 10^{-9}$,[21] $K_{b,dmf} = 1.5 \times 10^{-14}$ (ref. 22)] are in favour of the protonation of the ligand on the specific position of the hydrazone nitrogen, as shown in intermediate **B** in Scheme 1. More important seems to be the relative permittivity of the solvent for stabilising the cationic intermediate **C**, the solvent with the lowest value, pyridine, giving the worst catalytic activity. The homogeneity of the process is substantiated by the following elements: (a) the high observed chemoselectivity from a triple to a double bond that would be impossible for a reaction catalysed by traces of (colloidal) metal palladium;[23] (b) the catalytic activity of the complexes is strongly dependent on their solubility, **1a**, which is the least soluble complex in dmf, exhibiting the worst catalytic activity (Table 4, entry 1); (c) using thf as solvent, in which the chloro complexes are not soluble, no traces of styrene were found after 24 h of reaction.

Experimental

Synthesis

All manipulations were carried out in an atmosphere of purified, dry nitrogen by using standard Schlenk techniques. Solvents were dried and stored under nitrogen. Reagents were used without further purification. Thiobenzoylhydrazine was synthesized following a reported method.[24]

Proton NMR spectra were recorded on a Bruker 300 FT spectrometer using $SiMe_4$ as internal standard at 25 °C, IR spectra with a Nicolet 5PCFT-IR spectrophotometer in the 4000–400 cm^{-1} range by using KBr discs. The GC analyses were performed on a Dani HP 3800 flame-ionisation gas chromatograph (OV 101 on CHP column). Mass spectra were recorded on a FINNIGAN SSQ 710 spectrometer. Elemental analyses (C, H, N and S) were performed by using a Carlo Erba Model EA 1108 apparatus.

Ligands HL^1–HL^4 were synthesized by refluxing a solution containing the ketonic system (0.5 g) and the corresponding thiohydrazide in a 1:1 molar ratio, in the presence of some drops of glacial acetic acid as catalyst; HL^1 and HL^3 were isolated by slow evaporation of the solvent, HL^2 and HL^4 after cooling the solution at −10 °C overnight in the presence of diethyl ether (twofold with respect to the reaction solvent). Complexes **1–4** were synthesized by dropping a solution containing the palladium salt into a solution containing the ligand (0.1 g) in a 1:1 molar ratio at room temperature; **1a** and **1c** were isolated by slow evaporation of the solvent, the others being precipitated during the stirring. The reaction time and solvent, together with physical and analytical data of all the compounds, are summarised in Table 6. All the ligands were confirmed by CI mass spectrometry. In order to save space the coupling constants are not reported.

X-Ray crystallography

Well shaped single crystals suitable for X-ray diffractometric analysis were obtained for complexes **1a** (orange prisms) and **2**

Table 6 Employed experimental conditions for the synthesis of the ligands and complexes, together with physical and analytical data

						Analysis* (%)			
Compound	Solvent/cm^3	*t*/h	M.p./°C	Yield (%)	Colour	C	H	N	S
HL[1]	Methanol (80)	24	144–147	70	Pale yellow	60.7 (60.9)	4.85 (4.7)	21.7 (21.9)	12.8 (12.5)
HL[2]	Methanol (80)	120	175–176	67	Orange	71.8 (71.9)	4.75 (4.8)	13.15 (13.25)	10.0 (10.1)
HL[3]	Methanol (80)	15	157.5–159.3	79	Pale yellow	49.5 (49.5)	5.2 (5.2)	28.8 (28.8)	16.55 (16.5)
HL[4]	Abs. ethanol (80)	24	175.3–177.6	45	Orange	65.8 (65.85)	5.15 (5.1)	16.4 (16.5)	12.6 (12.6)
1a	Acetonitrile–methanol (30:20)	3	281–288.5 (decomp.)	92	Orange	39.6 (39.3)	3.0 (2.8)	14.0 (14.1)	8.1 (8.1)
1b	Acetonitrile (45)	3	266.4–274.6 (decomp.)	35	Orange	42.6 (42.8)	3.25 (3.35)	13.2 (13.3)	7.6 (7.6)
1c	Acetonitrile–acetone–water (20:10:1)	3	>300	65	Purple	31.8 (31.95)	2.2 (2.3)	11.3 (11.5)	6.6 (6.6)
2	Acetonitrile–methanol (30:20)	3	>300	75	Red	49.5 (49.8)	3.0 (3.1)	8.95 (9.2)	7.1 (7.0)
3	Methanol (90)	15	>300	86	Yellow	28.6 (28.7)	2.6 (2.7)	16.7 (16.7)	9.75 (9.6)
4	Methanol (90)	15	>300	91	Orange	42.7 (42.5)	3.0 (3.1)	10.3 (10.6)	8.1 (8.1)

* Required values are given in parentheses.

(red prisms)‡ by slow evaporation of the reaction solvent. In both cases the phase problem was solved by direct methods, using SIR 92.[25] Neutral atomic scattering factors were employed, those for non-hydrogen atoms being corrected for anomalous dispersion. Structures were refined by full-matrix least squares on F^2 with SHELXL 93.[26] The empirical method by Walker and Stuart[27] was applied to correct for absorption. Anisotropic displacement parameters were used for all non-hydrogen atoms. Hydrogen atoms were located on the Fourier-difference map and refined with isotropic displacement parameters for **1a**, while they were introduced at calculated positions, riding on their carrier atoms for **2**. The final geometry was analysed by the program PARST 95[28] and the drawings were made with ZORTEP.[29] All calculations were performed on an ENCORE 91 computer at the Centro di Studio per la Strutturistica Diffrattometrica del C.N.R. in Parma. Data for comparison with other compounds were retrieved and analysed by the software packages of the Cambridge Structural Database.[30]

CCDC reference number 186/1025.

See http://www.rsc.org/suppdata/dt/1998/2715/ for crystallographic files in .cif format.

Catalysis

All manipulations were carried out under purified dry nitrogen by using standard Schlenk techniques. Solvents were dried prior to use and stored under nitrogen. Styrene and phenylacetylene were distilled in vacuum and stored under nitrogen. The hydrogenating apparatus is equivalent to that previously reported.[1,2] The progress of the reaction was followed by withdrawing small portions of the reaction mixture at determined time intervals. These were passed over a short silica column to remove palladium complexes and possible traces of black palladium, then a quantitative determination was carried out by gas chromatography according to the internal standard method (1,3,5-trimethylbenzene). In order to use the initial rates method in the calculations we considered conversions up to 20%. The stirrer was operated in such a manner that there was no limitation due to diffusion control. Hydrogen pressures less than 1 atm were obtained by mixing at constant pressure and temperature in a gas burette exact volumes of hydrogen and nitrogen, keeping the gases in contact for 12 h. The solubility of hydrogen in dmf was considered to be constant for every run. The concentration of hydrogen was determined as a function of temperature and hydrogen pressure by the assumption of a linear dependence on $p(H_2)$.[31] Plots of kinetic data were fitted by the use of conventional linear regression programs to $r^2 \geqslant 0.96$.

At the end of the reaction the solution was conventionally worked up. The residue, containing the starting complex, was analysed by IR spectrophotometry to confirm the unchanged nature of the catalyst.

Hydrogenation

Of phenylacetylene. The complex (0.036 mmol; 0.014 g of **1a** and **4**, 0.015 g of **1b**, 0.017 g of **1c** and **2**, 0.012 g of **3**) was dissolved in dry solvent (25 cm^3); phenylacetylene (3.600 mmol, 0.368 g, 0.400 cm^3) and 1,3,5-trimethylbenzene (2.496 mmol, 0.300 g, 0.347 cm^3) were added to the solution which was thermostatted to the required temperature. After 24 h of reaction the composition of the solution was determined by GC.

Of styrene. The same procedure as above was employed.

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‡ Crystal data: for **1a**, $C_{13}H_{11}ClN_4PdS$, $M = 397.2$, monoclinic, space group $C2/c$, $a = 12.089(4)$, $b = 21.801(7)$, $c = 11.480(4)$ Å, $\beta = 108.35(3)°$, $U = 2872(2)$ Å^3, $Z = 8$, Siemens AED diffractometer, θ–2θ scan, $\lambda = 0.710\,78$ Å (Mo-Kα), $\mu = 16.8$ cm^{-1}, $T = 293$ K, $R1 = 0.0365$ for 3188 observed reflections [$I > 2\sigma(I)$] (4184 independent). For **2**, $C_{19}H_{14}ClN_3PdS$, $M = 458.2$, monoclinic, space group $P2_1/n$, $a = 12.235(3)$, $b = 9.413(2)$, $c = 15.670(4)$ Å, $\beta = 101.20(1)°$, $U = 1770(1)$ Å^3, $Z = 4$, Siemens AED diffractometer, θ–2θ scan, $\lambda = 0.710\,78$ Å (Mo-Kα), $\mu = 13.2$ cm^{-1}, $T = 293$ K, $R1 = 0.0685$ for 1227 observed reflections [$I > 2\sigma(I)$] (3140 independent).

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