Palladium(II) complexes containing a P, N chelating ligand Part II [1]. Synthesis and characterisation of complexes with different hydrazinic ligands. Catalytic activity in the hydrogenation of double and triple C–C bonds

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Abstract

Palladium(II) complexes of the type Pd(PNO)Y (PNO = 2-(diphenylphosphino)benzaldehyde picolinhydrazone, nicotinhydrazone, isonicotinhydrazone; Y = CH_3CO_2, Cl, I) and Pd(PNS)Y (PNS = 2-(diphenylphosphino)benzaldehyde thiosemicarbazone; Y = CH_3CO_2, Cl, I) were synthesised and characterised by spectroscopic methods. The X-ray structure of an iodo complex was also determined. The catalytic activity of all the complexes in the homogeneous hydrogenation of terminal double and triple bonds was tested with particular regards to the chemoselectivity from triple to double bond. A correlation between the catalytic activity and the nature of the ligand and Y group was established. In the hydrogenation of phenylacetylene using acetato complexes as catalysts, stable phenylethynylpalladium(II) complexes were recovered and characterised by spectroscopic methods. A facile route of synthesis of alkynyl complexes was also determined. © 1997 Elsevier Science S.A.

1. Introduction

Recently, we described the synthesis and characterisation of Pd(II) complexes containing a polyfunctional phosphino hydrazonic ligand named Hbidf (Fig. 1) [1], that is able to stabilise Pd(II) under catalytic hydrogenation conditions. The ligand can act like a hemilabile P, N, O terdentate as well as a P, N bidentate ligand, according to the concept of hemilabile ligands introduced by Jeffrey and Rauchfuss [2].

In particular the square planar Pd(bidf)(CH$_3$CO$_2$) complex (Fig. 1) is an active catalyst for hydrogenation of styrene under atmospheric pressure of hydrogen at room temperature. Moreover, our investigation emphasised the different behaviour of complex Pd(bidf)(CH$_3$CO$_2$) in the hydrogenation of styrene and

phenylacetylene. The former is catalytically reduced to ethylbenzene, the latter is partially reduced to styrene. In this case the catalytic process is broken off owing to the formation of a stable phenylethynylpalladium(II) complex which is very scarcely active in the hydrogenation reaction. In order to obtain more detailed information about the ability of the mentioned complexes in the activation of molecular hydrogen we have carried out a study on Pd(II) complexes containing modified phosphino hydrazinic ligands. We have thus designed new polyfunctional P, N, O and P, N, S ligands. In this paper we report the synthesis, characterisation and catalytic properties of a series of Pd(PNO)Y and Pd(PNS)Y complexes employed as hydrogenation catalysts for styrene and phenylacetylene, in relation to the reported results of Pd(bidf)Y complexes and with particular attention to the selective reduction of triple to double bonds, as has been recently observed for rhodium [3], ruthenium [4] and osmium [5] complexes. The crystal structure of the complex Pd(pidf)I · $\frac{1}{4}$CH$_3$CN and a

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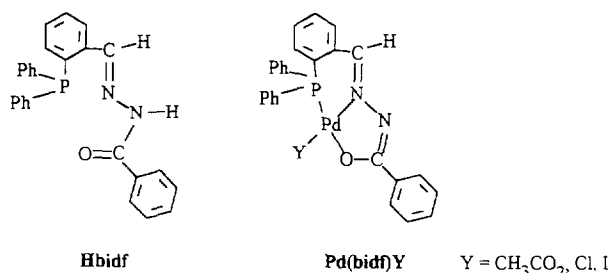
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[1] For Part I see Ref. [1].

Fig. 1. Hbidf ligand and related palladium(II) complexes.

facile route of synthesis of novel alkynylpalladium(II) complexes are also reported.

2. Results and discussion

2.1. Complexes

In all the palladium(II) complexes the hydrazone behaves as a terdentate ligand, giving rise to an essentially square planar structure, involving a six-membered ring with phosphorus and a five-membered ring with oxygen or sulphur, as shown in Fig. 2.

The coordination mode of the ligands to the metal centre through P, N, O or P, N, S, is proved by spectroscopic data (Table 1). In the IR spectra of the complexes the signal of the N–H bond present in the ligands (in the region 3295–3170 cm^{-1}) is always absent, indicating their deprotonation. For the P, N, O complexes the disappearance of the resonance of the C=O group (in the region 1699–1610 cm^{-1}) is indicative of the coordination through the carbonylic oxygen [6], while for the P, N, S complexes the shift to lower frequencies of the signal due to the stretching of the C=S and C–S bonds ($\Delta\nu = 55$ cm^{-1} and 64 cm^{-1} re-

spectively) denotes the presence of the Pd–S coordination [7]. In the IR spectra of the acetato complexes the asymmetric and symmetric stretchings of the carboxylic group are present to about 1620 cm^{-1} and 1320 cm^{-1} respectively for the coordination P, N, O and to 1584 cm^{-1} and 1325 cm^{-1} respectively for the coordination P, N, S, showing the characteristic values for a monodentate coordination of this anion to the metal centre [8].

The ^{1}H NMR spectra of the ligands show the signals of the N–H hydrazonic proton and the doublet of the CH=N proton with a phosphorus coupling constant of about 4 Hz [9–11], this latter signal being always present in the complexes.

The coordination through the phosphorus atom in the P, N, S complexes is clearly indicated by a chemical shift of the signal in the ^{31}P NMR spectra to higher fields than the signal of the free ligand [Δ(ppm):Pd(tsdf)(CH$_3$CO$_2$) = 35.52, Pd(tsdf)Cl = 33.72, Pd(tsdf)I = 35.72].

An X-ray diffraction analysis carried out on the Pd(pidf)I · $\frac{1}{4}$CH$_3$CN complex has confirmed the expected coordination.

From 2a–e (Y = CH$_3$CO$_2$) it was possible to prepare in high yields alkynylpalladium(II) complexes (3a–e) by direct reaction of acetate complexes with terminal alkynes, Eq. (1), under mild conditions in various solvents like methanol, toluene or THF.
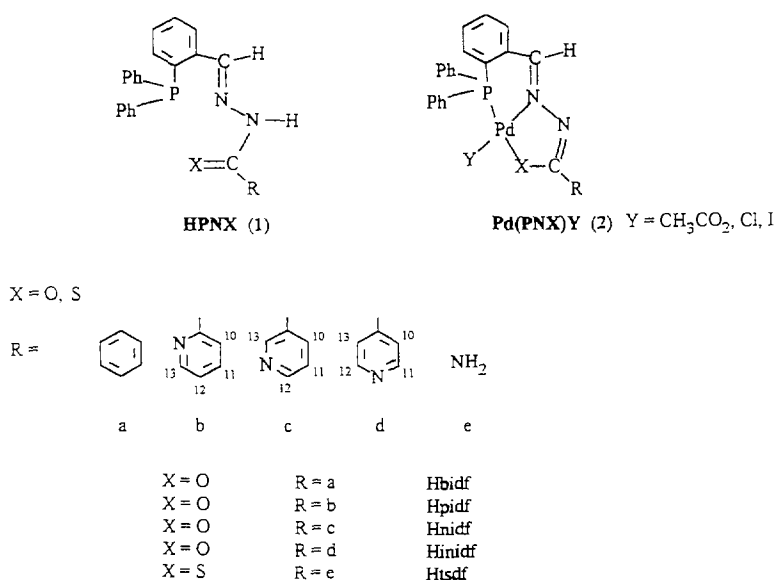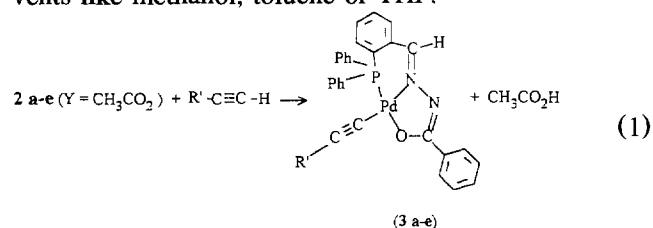

$$2 \text{ a-e } (Y = CH_3CO_2) + R'\text{-}C{\equiv}C\text{-}H \longrightarrow \quad + CH_3CO_2H \tag{1}$$

(3 a-e)

Fig. 2. Schemes of the ligands and the palladium complexes.

Table 1
Selected spectroscopic data [IR (cm^{-1}), ^{1}H NMR (ppm)] for ligands and complexes

Name	X	ν(N–H)	ν(C=X)	ν(CO$_2$)$_{asym}$	ν(CO$_2$)$_{sym}$	δ(N–H)	δ(CH=N)
Hbidf	O	3220$_{br}$	1652$_{vs}$	—	—	9.49$_s$	7.84$_d$
Pd(bidf)(CH$_3$CO$_2$)	O	—	—	1573$_{br}$	1322$_m$	—	8.25$_d$
Pd(bidf)Cl	O	—	—	—	—	—	8.41$_d$
Pd(bidf)I	O	—	—	—	—	—	8.38$_d$
Hpidf	O	3295$_w$	1699$_{vs}$	—	—	10.94$_s$	8.56$_d$
Pd(pidf)(CH$_3$CO$_2$)	O	—	—	1623$_m$	1324$_m$	—	8.48$_d$
Pd(pidf)Cl	O	—	—	—	—	—	8.66
Pd(pidf)I	O	—	—	—	—	—	8.54$_d$
Hnidf	O	3198$_{br}$	1648$_{vs}$	—	—	10.12$_s$	8.71$_d$
Pd(nidf)(CH$_3$CO$_2$)	O	—	—	1623$_m$	1321$_m$	—	8.89$_d$
Pd(nidf)Cl	O	—	—	—	—	—	8.65$_d$
Pd(nidf)I	O	—	—	—	—	—	8.61$_d$
Hinidf	O	3193$_{br}$	1649$_{vs}$	—	—	10.17$_s$	8.64$_d$
Pd(inidf)(CH$_3$CO$_2$)	O	—	—	1617$_s$	1319$_m$	—	8.31$_d$
Pd(inidf)Cl	O	—	—	—	—	—	8.44$_d$
Pd(inidf)I	O	—	—	—	—	—	8.33$_d$
Htsdf	S	3170$_{ms}$	1273$_{br}$	—	—	9.45$_s$	8.31$_d$
Pd(tsdf)(CH$_3$CO$_2$)	S	—	1214$_w$	1584$_{br}$	1325$_s$	—	7.93$_d$
Pd(tsdf)Cl	S	—	1222$_w$	—	—	—	8.17$_d$
Pd(tsdf)I	S	—	1218$_w$	—	—	—	8.13$_d$

The proposed route of synthesis is easier than those reported in the literature; these in fact, often provide an oxidative addition of an alkynylhalide to a palladium(0) complex [10], a metathetic exchange between halopalladium(II) complex and Li(C≡C–R') [12] or deprotonation of the acetylenic molecule by a base [13]. The high stability of the isolated alkynyl complexes 3a–e, Eq. (1), allowed their complete characterisation; the elemental analysis was in good accord with theoretical values also after a long time of exposure to air and light, pointing out no decomposition. These alkynyl complexes were stable after refluxing for a long time in methanol or toluene. Although the X-ray structure de-termination of 3a–e complexes could not be carried out, since no crystals suitable for an X-ray diffraction analysis were obtained, the comparison of their spectroscopic data with those of the previously reported alkynylpalladium(II) complexes [1] justifies the assigned square planar coordination through the P, N, O or P, N, S atoms of the ligands. Thus the presence of the C≡C group in 3a–e complexes is proved by the signal in the IR spectra at about 2120 cm^{-1} and by the consequent disappearance of the signals due to the acetato group. The five aromatic protons of the phenylacetylene are present in the ^{1}H NMR spectrum to higher field than those of the phosphino group.
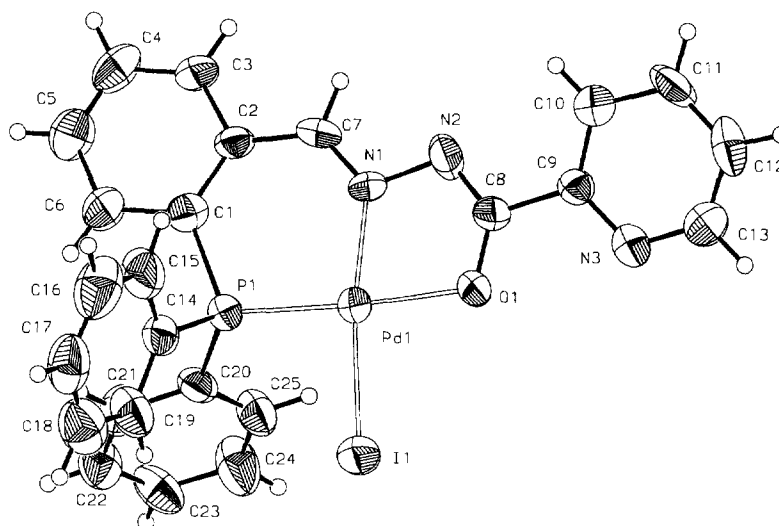

Fig. 3. ORTEP diagram for Pd(pidf)I (molecule A). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are represented by arbitrarily small spheres.

2.2. X-ray structure of Pd(pidf)I · ¼CH₃CN

The asymmetric unit contains two crystallographically independent Pd(pidf)I complex molecules, the drawings of which are shown in Figs. 3 and 4, and half a molecule of acetonitrile which exhibits a crystallographically imposed two-fold symmetry with all non-hydrogen atoms lying on a two-fold axis. The main structural parameters are listed in Table 2. In both molecules the palladium atom is in the centre of a square planar arrangement formed by three atoms (P, O, N) from the pidf ligand and an iodine atom. The coordination of pidf to palladium produces two chelate rings, one six- and the other five-membered.

The title structure is strictly related to that of Pd(L)Cl [1], from which it differs in the nature of the halogen and in the presence in the organic ligand of a pyridine instead of a phenyl ring. No structures for palladium(II) compounds containing the same ligand arrangement (i.e. P, O, N and I) as in the present complex have been so far reported in the Cambridge Crystallographic Database. The Pd–P, Pd–O and Pd–N distances agree fairly well with those found in the above-mentioned Pd(L)Cl, whereas the Pd–I distances are about 0.03 Å shorter than those observed for Pd(HL)I [6]. As shown in Fig. 5, the two independent molecules are linked through CH · · · O hydrogen bonds (C24–H · · · O2 (3.27(3) Å, 128(2)°) and C32–H · · · O1 (3.29(2) Å, 142(2)°)) which give rise to a dimeric structure. The two molecules are not equivalent as far as the intermolecular contacts are concerned, since different donors are involved in the formation of the dimer, namely a phenylic C–H for molecule A and the ethylenic C–H for molecule B. In

Table 2
Selected bond distances (Å) and angles (deg) with e.s.d.s in parentheses

| Pd1–I1	2.568(2)	Pd2–I2	2.575(2)
Pd1–P1	2.212(4)	Pd2–P2	2.195(5)
Pd1–O1	2.06(1)	Pd2–O2	2.08(1)
Pd1–N1	1.99(1)	Pd2–N4	2.03(1)
P1–C1	1.84(2)	P2–C26	1.85(1)
P1–C14	1.82(2)	P2–C39	1.79(2)
P1–C20	1.83(1)	P2–C45	1.80(2)
O1–C8	1.28(2)	O2–C33	1.27(2)
N1–N2	1.41(2)	N4–N5	1.42(2)
N1–C7	1.29(2)	N4–C32	1.25(2)
N2–C8	1.29(2)	N5–C33	1.33(2)
N3–C9	1.33(2)	N6–C34	1.33(2)
N3–C13	1.34(2)	N6–C38	1.34(3)
C2–C7	1.45(2)	C27–C32	1.49(2)
C8–C9	1.51(2)	C33–C34	1.48(2)
O1–Pd1–N1	79.3(4)	O2–Pd2–N4	80.0(5)
P1–Pd1–N1	96.8(4)	P2–Pd2–N4	92.6(4)
P1–Pd1–O1	175.8(3)	P2–Pd2–O2	166.5(3)
I1–Pd1–N1	171.3(4)	I2–Pd2–N4	171.3(4)
I1–Pd1–O1	92.1(3)	I2–Pd2–O2	94.1(3)
I1–Pd1–P1	91.8(1)	I2–Pd2–P2	94.5(1)
Pd1–P1–C20	115.7(5)	Pd2–P2–C45	121.1(6)
Pd1–P1–C14	114.8(5)	Pd2–P2–C39	106.8(5)
Pd1–P1–C1	110.2(5)	Pd2–P2–C26	111.4(5)
C14–P1–C20	106.9(8)	C39–P2–C45	108.3(8)
C1–P1–C20	104.0(8)	C26–P2–C45	103.7(8)
C1–P1–C14	104.2(8)	C26–P2–C39	104.4(8)
Pd1–O1–C8	108(1)	Pd2–O2–C33	109(1)
Pd1–N1–C7	132(1)	Pd2–N4–C32	132(1)
Pd1–N1–N2	114(1)	Pd2–N4–N5	112(1)
N2–N1–C7	114(1)	N5–N4–C32	115(1)
N1–N2–C8	110(1)	N4–N5–C33	112(1)
N1–C7–C2	128(1)	N4–C32–C27	128(1)
O1–C8–N2	128(1)	O2–C33–N5	126(1)
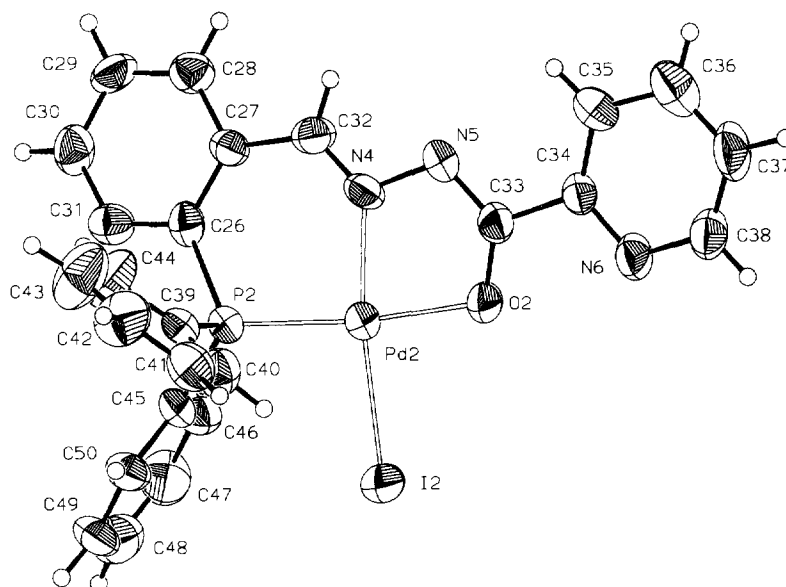
Fig. 4. ORTEP diagram for Pd(pidf)I (molecule B). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are represented by arbitrarily small spheres.
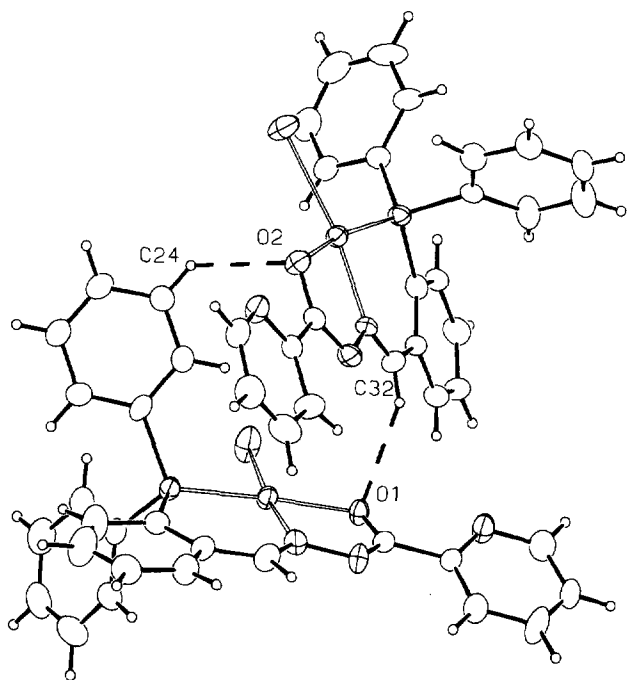
Fig. 5. Structural representation of the dimeric unit of Pd(pidf)I.

both cases the acceptors are the carbonyl oxygens. The corresponding ethylenic C–H in molecule A (C7) does not participate in any intermolecular interaction, while C40–H of molecule B is hydrogen-bonded to the aceto-nitrile molecule (C40–H · · · N7 = 3.28(2) Å, 129(2)°). Being on the two-fold axis, the acetonitrile molecule bridges two symmetry-related dimers (Fig. 6). The interaction with acetonitrile involves only molecule B and is likely to induce a distortion in the coordination of palladium as well as to affect bond geometry of the hydrazonic backbone from C27 to C34. The –P(Ph)$_2$ group of molecule B is pulled towards the two-fold axis by the hydrogen bond between one phenyl and aceto-nitrile, consequently P2 is displaced by 0.6 Å from the square planar arrangement around Pd2, and the angle Pd–P–O decreases to 166.5°, while in molecule A, which displays an exact square planar coordination, it is 175.8°. The overall tetrahedral distortion in the coordi-
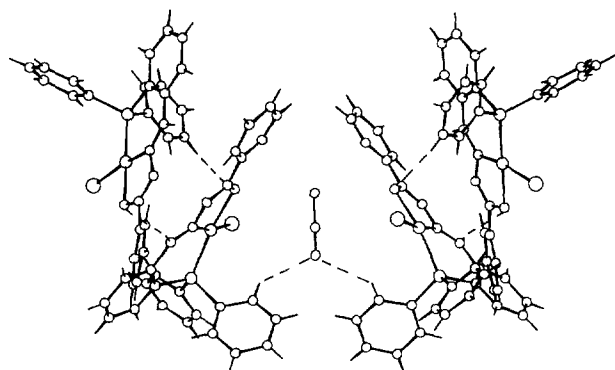

Fig. 6. Crystal packing in Pd(pidf)I · ¼CH$_3$CN.

Table 3
Comparison of contributions to conformational energy for molecules A and B

	Energy (kcal mol^{-1})	
	Molecule A	Molecule B
Bond stretching energy	1.257	2.583
Angle bending energy	7.034	10.661
Torsional energy	16.566	15.856
Out-of-plane bending energy	0.373	2.226
1–4 van der Waals energy	7.406	7.216
Van der Waals energy	– 4.994	– 7.472
Total energy	27.643	31.070

nation of Pd2 affects also the ligand geometry of molecule B. The C(H)–N bond is shorter in B than in A (1.25(2) Å vs. 1.29(2) Å respectively) whereas the reverse occurs for the adjacent N–N bond (1.42(2) Å in B and 1.41(2) Å in A) and Ph–C bond (1.49(2) Å in B and 1.45(2) Å in A). Even if these differences are not highly significant when taken singularly, their simultaneous occurrence supports the hypothesis that the molecular deformation observed for B induces a non-negligible rearrangement of the bond strengths in the hydrazonic moiety. The energetic expense for the overall deformation of molecule B is approximately 3.5 kcal mol^{-1}, as evidenced in Table 3 by the comparison of conformational energies for molecule A and B carried out by the program SYBYL using default parameters for the Tripos force-field and charges evaluated according to Gesteiger and Marsili [14]. It has been shown [15] that C–H · · · O and C–H · · · N hydrogen bonds may contribute to crystal stabilisation by an amount as large as 4 kcal mol^{-1} and that C · · · N, O interactions of 3.4–3.5 Å can drive the crystal packing of organic compounds, even in the presence of stronger hydrogen bond donors as O–H and N–H groups. In the present structure only C–H donors are available and the formation of rather short hydrogen bonds is likely to compensate the energy loss required for the slight but significant conformational differentiation of the two chemically equivalent molecules.

2.3. Catalysis

Complexes 2a–e (Y = CH$_3$CO$_2$, Cl, I) were utilised for catalytic hydrogenation of styrene and phenylacety-lene at 25 °C and at atmospheric pressure of hydrogen in methanol as solvent. The results reported in Tables 4 and 5 can be considered as an activity test of the different catalysts. These data were all obtained under the same reaction conditions and concern the time for total conversion or the percent conversion and yields after a fixed reaction time. The results point out that the hydrazonic complexes of type Pd(PNS)Y under the reported experimental conditions, do not show any ability to hydrogenate styrene and phenylacetylene indepen-

Table 4
Hydrogenation data for styrene

Entry	Pd complex	Time (h)	Styrene (%)	Ethylbenzene (%)
1	Pd(bidf)(CH₃CO₂)	24	—	100
2	Pd(pidf)(CH₃CO₂)	48	80	20
3	Pd(nidf)(CH₃CO₂)	32	—	100
4	Pd(inidf)(CH₃CO₂)	18	—	100
5	Pd(tsdf)(CH₃CO₂)	24	100	—
6	Pd(bidf)Cl	48	100	—
7	Pd(pidf)Cl	48	99	1
8	Pd(nidf)Cl	48	95	5
9	Pd(inidf)Cl	48	77	23
10	Pd(tsdf)Cl	48	100	—
11	Pd(bidf)I	48	100	—
12	Pd(pidf)I	48	100	—
13	Pd(nidf)I	48	100	—
14	Pd(inidf)I	48	98	2
15	Pd(tsdf)I	48	100	—

dently on the nature of the anionic ligands Y (Table 4 entries 5, 10 and 15; Table 5 entries 5, 11 and 14). Pd(PNO)Y complexes, instead, promoted the catalytic hydrogenation of styrene and phenylacetylene. The catalytic efficiency is strongly influenced by the nature of the Y ligand and to a lesser extent by the nature of the R group of the hydrazonic ligand. As with styrene the hydrogenating ability depends on the Y ligand and the results in Table 4 show the following order: $CH_3CO_2 \gg Cl$ while I is not at all active. For a determined anionic group Y the activity of the catalyst is tuned by the nature of the R group of the P, N, O ligand. Thus when $Y = CH_3CO_2$ the order of activity is: inidf > bidf > nidf ≫ pidf; when Y = Cl the order is: inidf > nidf > pidf (no activity for bidf); inidf resulted the ligand with the highest catalytic activities for both the anionic ligands Y. In no way, under the reported conditions, can

the variation of the R group reverse the hydrogenation ability given by the Y group (see results in Table 4). In all cases at the end of the reaction the starting complexes were recovered. The data concerning the hydrogenation of phenylacetylene reported in Table 5 show close analogies with those of the styrene. The dependence of the hydrogenating ability is limited not only to $Y = CH_3CO_2$ but it is extended to Y = Cl in accord with the following order $CH_3CO_2 \approx Cl \gg I$. Also in this case the complexes with the inidf ligand gave the highest activity with both CH_3CO_2 and Cl groups. The hydrogenation of phenylacetylene involves chemoselectivity to styrene and ethylbenzene. The results obtained point out that this phenomenon is governed by the nature of Y and R groups. When $Y = CH_3CO_2$ no chemoselectivity was observed, except for the case of Pd(pidf)(CH₃CO₂) (entry 2 Table 5) and a mixture of styrene and ethylbenzene was obtained. On the contrary, with Y = Cl a high chemoselectivity to styrene was observed except for Pd(nidf)Cl (entry 9 Table 5); Pd(inidf)Cl yielded again the best activity and selectivity. Using Pd(PNO)(CH₃CO₂) as catalyst the crude reaction mixture contained CH_3CO_2H and consequently stable phenylethynylpalladium(II) complexes were recovered. The presence of the pyridinic ring made these alkynyl complexes soluble in the medium of reaction and this allowed complete conversion of the substrate (entries 2, 3 and 4, Table 5), unlike the alkynylpalladium(II) complexes originated from Pd(bidf)(CH₃CO₂) (entry 1, Table 5) which, owing to its insolubility, was not able to carry out the reaction to completeness [1]. Formation of alkynyl complexes was also observed in the attempt to hydrogenate phenylacetylene in the presence of Pd(tsdf)(CH₃CO₂) as catalyst, which was, however, inactive (entry 5, Table 5). Iodide complexes showed no or very small activity, giving in every case only styrene;

Table 5
Hydrogenation data for phenylacetylene

Entry	Pd complex	Time (h)	Ph–C≡C–H (%)	Ph–CH=CH₂ (%)	Ph–CH₂–CH₃ (%)	Recovered complex
1	Pd(bidf)(CH₃CO₂)	24	50	50	—	alkynyl complex
2	Pd(pidf)(CH₃CO₂)	42	—	90	10	alkynyl complex
3	Pd(nidf)(CH₃CO₂)	32	—	42	58	alkynyl complex
4	Pd(inidf)(CH₃CO₂)	18	—	54	46	alkynyl complex
5	Pd(tsdf)(CH₃CO₂)	48	96	4	—	alkynyl complex
6	Pd(bidf)Cl	24	66	31	2	starting complex
7	Pd(pidf)Cl	36	—	88	12	starting complex
8	Pd(pidf)Cl + NR₄Cl	72	48	52	—	starting complex
9	Pd(nidf)Cl	48	7	72	21	starting complex
10	Pd(inidf)Cl	24	—	92	8	starting complex
11	Pd(tsdf)Cl	48	100	—	—	starting complex
12	Pd(bidf)I	48	95	5	—	starting complex
13	Pd(pidf)I	48	100	—	—	starting complex
14	Pd(nidf)I	48	100	—	—	starting complex
15	Pd(inidf)I	48	88	12	—	starting complex
16	Pd(tsdf)I	48	100	—	—	starting complex

chloro and iodo complexes were always recovered unchanged after the hydrogenation reaction.

Taking into account the structure of the complexes 2a–e it is possible to advance a rationalisation of their catalytic behaviour. All the ligands have basic sites; in particular, the hydrazonic nitrogen was the most basic one (see Table 6). Thus it seems that the activation of the molecular hydrogen occurs by heterolytic cleavage [16] with protonation of hydrazonic nitrogen and formation of an as yet not isolated palladium hydride complex, rather than an oxidative addition with formation of a palladium(IV) hydride species.

This implies the formation of an ionic intermediate by removal of the Y group from the coordination sphere of the metal (structure 4, Eq. (2)). The observed reactivity order, $CH_3COO > Cl \gg I$, is in relation to the effectiveness of the good leaving group that decreases, for the palladium complexes, from acetate to iodide.


(4)   (5)
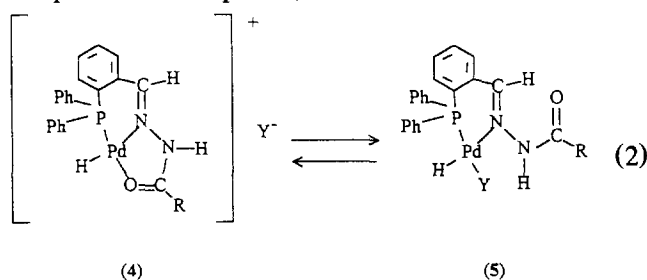
The structure 4 allows the coordination of the styrene molecule by breaking of the Pd–O bond while in the structure 5 this is prevented owing to the presence of the Y group bonded to the palladium atom again. This latter structure would be present in excess using halogen complexes.

On the contrary, phenylacetylene forming a more stable π-intermediate complex is able to coordinate to palladium removing the Cl group as an anion. This hypothesis is confirmed by a decreasing of the reaction rate when in solution was present an excess of Cl anions (entry 8, Table 5).

The importance of the presence of a labile coordination site is confirmed by the idleness of the complexes

containing P, N, S atoms, where two strong coordinating bonds like Pd–P and Pd–S do not permit the coordination of unsaturated molecules even in the presence of the best leaving group CH_3CO_2. It is worth noting that the lack of hydrogenation ability cannot be attributed to the incapability of forming the hydride species since the $Pd(tsdf)(CH_3CO_2)$ complex easily activates the C–H bond of phenylacetylene, giving the alkynylpalladium(II) complex and CH_3CO_2H.

The complete inactivity of the iodo complexes also excludes the possibility of a fifth coordination on the palladium atom. The lower catalytic activity observed for the acetate (entries 2, Tables 4 and 5) and chloro complexes (entry 7, Table 4) of Hpidf in the hydrogenation of styrene is due to the possibility of coordination by pyridinic nitrogen after protonation of the ligand as shown in Eq. (3).

(3)
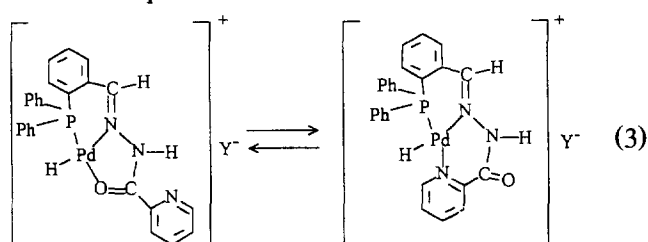
The exclusion by the coordination of the carbonylic group was demonstrated by us in palladium(II) complexes with phenyl-2-pyridylketone benzoylhydrazone [6], where a phenyl ring was preferred to the carbonylic oxygen and in a work of Vrieze and coworkers [11] with a multifunctional and hemilabile phosphino-imino-pyridyl ligand containing the 2-(diphenylphosphino)benzaldehyde. This event introduces a further obstacle to the coordination of the double bond and consequently a slowing down of the hydrogenation reaction was observed. In the case of phenylacetylene the competition between the coordination Pd–py and πPd–(C–C triple bond) is stronger than with styrene, the triple bond is more easily coordinated and then hydrogenated with a good chemoselectivity (entries 2 and 7 in Tables 4 and 5).

Table 6
Protonation constants ($\log \beta_{11}$) of hydrazonic nitrogen for the different ligands from absorbance data (230–430 nm) with the program SQUAD. Temperature 25 °C; ionic strength, $I = 0.1 \, mol \, dm^{-3}$ (KCl)

Ligand	Hbidf	Hpidf	Hnidf	Hinidf	Htsdf
$\log \beta_{11}$	12.34(1)	12.63(1)	11.31(1)	10.99(1)	12.42(2)
U	7.145×10^{-2}	3.180×10^{-2}	6.924×10^{-2}	3.363×10^{-2}	7.136×10^{-3}
σ_{tot}	8.436×10^{-3}	4.194×10^{-3}	7.580×10^{-3}	4.313×10^{-3}	3.142×10^{-3}
N_p	1407	2211	1608	2211	1206
pH (range)	7.15–12.85	4.49–12.51	6.83–12.10	4.63–11.74	6.33–12.65

$\sigma_{tot} = [\Sigma w_i(A_c - A_o)^2/(NBA(NUMPH - JQ) - NCV)]^{1/2}$; $U = [\Sigma w_i(A_c - A_o)^2]$ where NBA = number of wavelengths (λ), NUMPH = number of solutions, JQ = number of ε to be calculated, NCV = number of protonation constant to be refined, w_i = unit weigth. N_p = number of points data used in the refinement.

On the basis of the results we think that the mechanism of hydrogenation of the alkenes and alkynes can be essentially analogous. After a π coordination of double or triple bond to palladium the hydride is transferred to the coordinated substrate forming an alkyl or alkenyl complex; the second hydrogen atom is successively transferred to metallo-organic intermediate that is removed allowing the restoration of the Pd(PNO)Y species.

A more complicated matter is the effect of the R group on the catalytic activity. A linear correlation between the basicity of the hydrazonic nitrogen and the reaction rate does not exist as it is deduced from log β_{11} of the ligands and the activity data. The best activity was found for the catalysts containing the Hinidf ligand that has the lowest hydrazonic nitrogen basicity, however. It may be supposed that a weakening of the Pd–O bond and the consequent coordination of the unsaturated substrate plays a prominent role in the reaction course and this could be influenced by the position of the pyridinic nitrogen through an electrowithdrawing effect; this effect is more marked when the nitrogen is in ortho or para position to the carbonyl group. In the former case the electrowithdrawing effect is counterbalanced by the coordination Pd–py, while in the latter case there is only the effect favourable to the catalysis.

3. Conclusions

The behaviour as hemilabile terdentate as well as bidentate ligands of hydrazonic derivatives containing different donors such as P, N and O or S has proved to be fruitful in providing free coordination sites under the appropriate conditions of hydrogenation on the palladium complexes. The hydrogenation ability depends on the capacity of the coordination of the unsaturated C–C bonds governed by the nature of the Y ligand. Chemoselectivity may be attributed either to the inability of the intermediate styrene formed in the hydrogenation of phenylacetylene to coordinate to palladium due to the nature of the Y ligand or to a change in the hydrogenation rate of phenylacetylene in comparison with styrene, due to the R group in the hydrazonic ligand. Further studies are in progress to design more effective ligands able to promote higher chemoselectivity with acetylenic substrates.

4. Experimental section

4.1. Materials and apparatus

Reagents and solvents were standard-grade products and were used without further purification. 2-(Diphenylphosphino)benzaldehyde was purchased from Aldrich-

Chemie. The hydrazidic systems were synthesised by 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 were recorded on a Finnigan SSQ 710 spectrometer. All the ligands were obtained by condensation of the hydrazide substrates with 2-(diphenylphosphino)benzaldehyde using methods similar to those reported for the preparation of hydrazonic ligands [1,2,17].

4.2. Synthesis of the ligands Hpidf, Hnidf, Hinidf

A solution of 2-(diphenylphosphino)benzaldehyde (0.1 g, 0.343 mmol) in cold dichloromethane (20 ml) containing some drops of glacial acetic acid was added at room temperature to a solution of the corresponding hydrazide (0.047 g, 0.343 mmol) in cold methanol. The yellow solution was then refluxed for 8 h obtaining a colourless solution. For slow evaporation of the solvent a colourless solid formed which was filtered and washed with Et$_2$O.

4.2.1. Hpidf (2-(diphenylphosphino)benzaldehyde picolinhydrazone)

M.p.: 135–136 °C; yield: 75%. MS/CI: m/z (relative intensity) 410 ([M + 1]$^+$, 100), 288 (25), 123 (9), 106 (69). Anal. Found: C, 73.39; H, 5.09; N, 10.08. C$_{25}$H$_{20}$N$_3$OP calc.: C, 73.34; H, 4.92; N, 10.26%. FT-IR cm^{-1}: ν(N–H) = 3295$_w$, ν(C–H)$_{arom.}$ = 3053$_w$, ν(C=O) = 1699$_{vs}$–1685$_{ms}$, ν(C=C)$_{arom.}$ = 1619$_w$, ν(C=N) = 1588$_m$, ν(C–P) = 1435$_{vs}$. ^{1}H NMR (CDCl$_3$, 25 °C): δ 10.94(s, 1 H, N–H), 9.05(d, 1 H, H$_{13}$, J(ortho) = 6 Hz), 8.56(d, 1 H, CH=N, J(P–H) = 4.5 Hz), 8.35(t, 1 H, H$_{11}$, J(ortho) = 6 Hz), 8.29(d, 1 H, H$_{10}$, J(ortho) = 8 Hz), 7.87(t, 1 H, H$_{12}$, J(ortho) = 8 Hz), 7.48–6.91(m, 14 H, Ph); ^{31}P NMR (DMSO-d_6, 25 °C): δ −12.00.

4.2.2. Hnidf (2-(diphenylphosphino)benzaldehyde nicotinhydrazone)

M.p.: 174–176 °C; yield: 73%. MS/CI: m/z (relative intensity) 410 ([M + 1]$^+$, 71), 288 (100), 106 (10). Anal. Found: C, 73.00; H, 4.89; N, 10.10. C$_{25}$H$_{20}$N$_3$OP calc.: C, 73.34; H, 4.92; N, 10.26%. FT-IR cm^{-1}: ν(N–H) = 3198$_{br}$, ν(C–H)$_{arom.}$ = 3058$_w$, ν(C=O) = 1648$_{vs}$, ν(C=C)$_{arom.}$ = 1610$_w$, ν(C=N) = 1592$_m$, ν(C–P) = 1438$_{ms}$. ^{1}H NMR (CDCl$_3$, 25 °C): δ 10.12(s, 1 H, N–H), 9.30(sbr, 1 H, H$_{13}$), 9.02(sbr, 1 H, H$_{12}$), 8.71(d, 1 H, CH=N, J(P–H) = 4 Hz), 8.20(d, 1 H, H$_{10}$,

J(ortho) = 8 Hz), 7.33–7.21(m, 14 H, Ph), 6.90(t, 1 H, H_{11}, J(ortho) = 7 Hz); ^{31}P NMR (DMSO-d_6, 25 °C): δ −11.96.

4.2.3. Hinidf (2-(diphenylphosphino)benzaldehyde isonicotinhydrazone)

M.p.: 179–180 °C; yield, 50%. MS/CI: m/z (relative intensity) 410 ([M + 1]$^+$, 100), 288 (45). Anal. Found: C, 73.35; H, 4.86; N, 10.15. $C_{25}H_{20}N_3OP$ calc.: C, 73.34; H, 4.92; N, 10.26%. FT-IR cm^{-1}: ν(N–H) = 3193$_{br}$, ν(C–H)$_{arom.}$ = 3053$_m$, ν(C–O) = 1649$_{vs}$, ν(C=C)$_{arom.}$ = 1610$_w$, ν(C=N) = 1585$_w$, ν(C–P) = 1434$_{vs}$. ^{1}H NMR(CDCl$_3$, 25 °C): δ 10.17(s, 1 H, N–H), 9.02(d, 2 H, H_{12}–H_{11}, J(ortho) = 6 Hz), 8.64(d, 1 H, CH=N, J(P–H) = 4 Hz), 7.67(d, 2 H, H_{13}–H_{10}, J(ortho) = 6 Hz), 7.48–6.65(m, 14 H, Ph); ^{31}P NMR (DMSO-d_6, 25 °C): δ −12.05.

4.3. Synthesis of the ligand Htsdf

A solution of 2-(diphenylphosphino)benzaldehyde (0.3 g, 1.033 mmol) was dissolved in hot methanol (50 ml) containing some drops of glacial acetic acid and was added to a methanolic solution (20 ml) of thiosemicarbazide (0.063 g, 0.691 mmol) and refluxed for 18 h until a colourless solution was obtained. For slow evaporation of the solvent a colourless microcrystalline product was filtered and washed with Et$_2$O.

4.3.1. Htsdf (2-(diphenylphosphino)benzaldehyde thiosemicarbazone)

M.p.: 220–222 °C; yield, 96%. MS/CI: m/z (relative intensity): 364 ([M + 1]$^+$, 4.9), 288 (100), 208 (4), 183 (7.3), 165 (4). Anal. Found: C, 65.98; H, 4.99; N, 11.44; S, 8.78. $C_{20}H_{18}N_3PS$ calc.: C, 66.10; H, 4.99; N, 11.56; S, 8.82%. FT-IR cm^{-1}: ν(NH$_2$)$_{asym.}$ = 3442$_m$, ν(NH$_2$)$_{sym.}$ = 3308$_m$, ν(N–H) = 3170$_m$, ν(C–H)$_{arom.}$ = 3025$_w$, ν(C=N) + δ(NH$_2$) = 1588$_s$, ν(C–P) = 1433$_m$, ν(C=S) = 1273$_{br}$, ν(C–S) = 812$_m$. ^{1}H NMR(CDCl$_3$, 25 °C): δ 9.45(s, 1 H, N–H), 8.31(d, 1 H, CH=N, J(P–H) = 4 Hz), 7.79–6.64(m, 14 H, Ph), 6.16(s, 2 H, NH$_2$); ^{31}P NMR (DMSO-d_6, 25 °C): δ −9.22.

4.4. Synthesis of the complexes Pd(pidf)Y, Pd(nidf)Y, Pd(inidf)Y (Y = CH_3CO_2, Cl, I)

A solution of the ligand (0.1 g, 0.244 mmol) in cold dichloromethane (30 ml) was slowly added to a solution containing the palladium salt [Pd(CH$_3$CO$_2$)$_2$ (0.049 g, 0.218 mmol) in acetonitrile (30 ml), K$_2$PdCl$_4$ (0.039 g, 0.220 mmol) in acetonitrile–water (25 ml/15 ml), K$_2$PdI$_4$ (0.079 g, 0.169 mmol) in acetone–water (30 ml/20 ml)]. The resultant solution was stirred at room temperature for 3 h. After slow evaporation of the solvent a microcrystalline product was isolated.

4.4.1. Pd(pidf)(CH$_3$CO$_2$)

Yellow; m.p.: 250–255 °C (dec.); yield, 90%. Anal. Found: C, 56.49; H, 3.81; N, 7.12. $C_{27}H_{22}N_3O_3PPd$ calc.: C, 56.51; H, 3.86; N, 7.32. FT-IR cm^{-1}: ν(C–H)$_{arom.}$ = 3055$_w$, ν(CO$_2$)$_{asym.}$ = 1623$_m$, ν(C=C)$_{arom.}$ = 1600$_s$, ν(C=N) = 1583$_s$, ν(C–P) = 1435$_s$, ν(CO$_2$)$_{sym.}$ = 1324$_m$. ^{1}H NMR (CDCl$_3$, 25 °C): δ 8.66(dd, 1 H, H_{13}, J(ortho) = 5 Hz, J(meta) = 1 Hz), 8.48(d, 1 H, CH=N, J(P–H) = 4 Hz), 8.27(d, 1 H, H_{10}, J(ortho) = 8 Hz), 7.78–7.44(m, 16 H, Ph and H_{12}–H_{11}), 1.64(s, 3 H, CH$_3$CO$_2$).

4.4.2. Pd(nidf)(CH$_3$CO$_2$)

Yellow; m.p.: 243–245 °C (dec.); yield, 80%. Anal. Found: C, 56.55; H, 3.79; N, 7.22. $C_{27}H_{22}N_3O_3PPd$ calc.: C, 56.51; H, 3.86; N, 7.32%. FT-IR cm^{-1}: ν(C–H)$_{arom.}$ = 3062$_w$, ν(CO$_2$)$_{asym.}$ = 1623$_m$, ν(C=C)$_{arom.}$ = 1600$_s$, ν(C=N) = 1583$_s$, ν(C–P) = 1437$_m$, ν(CO$_2$)$_{sym.}$ = 1321–1299$_m$. ^{1}H NMR (DMSO-d_6, 25 °C): δ 9.44(s, 1 H, H_{13}), 8.89(d, 1 H, CH=N, J(P–H) = 4 Hz), 8.69(m, 3 H, H_{12}–H_{11}–H_{10}), 8.20–7.21(m, 14 H, Ph), 1.91(s, 3 H, CH$_3$CO$_2$).

4.4.3. Pd(inidf)(CH$_3$CO$_2$)

Yellow; m.p.: 272–277 °C (dec.); yield, 90%. Anal. Found: C, 56.51; H, 3.96; N, 7.27. $C_{27}H_{22}N_3O_3PPd$ calc.: C, 56.51; H, 3.86; N, 7.32%. FT-IR cm^{-1}: ν(C–H)$_{arom.}$ = 3073–3034$_w$, ν(CO$_2$)$_{asym.}$ = 1617$_s$, ν(C=C)$_{arom.}$ = 1603$_s$, ν(C=N) = 1583$_s$, ν(C–P) = 1436$_m$, ν(CO$_2$)$_{sym.}$ = 1319$_m$. ^{1}H NMR (CDCl$_3$, 25 °C): δ 8.64(dbr, 2 H, H_{12}–H_{11}), 8.31(d, 1 H, CH=N, J(P–H) = 4.5 Hz), 7.96(d, 2 H, H_{13}–H_{10}, J(ortho) = 5 Hz), 7.74–7.36(m, 14 H, Ph), 1.66(s, 3 H, CH$_3$CO$_2$).

4.4.4. Pd(pidf)Cl

Yellow; m.p.: 286–292 °C (dec.); yield, 80%. Anal. Found: C, 48.25; H, 4.24; N, 6.75. $C_{25}H_{19}ClN_3OPPd \cdot 4H_2O$ calc.: C, 48.25; H, 4.37; N, 6.75%. FT-IR cm^{-1}: ν(C–H)$_{arom.}$ = 3056$_w$, ν(C=C)$_{arom.}$ = 1609$_w$, ν(C=N) = 1573$_w$, ν(C–P) = 1435$_s$. ^{1}H NMR (CDCl$_3$, 25 °C): δ 8.66(dbr, 2 H, H_{13} and CH=N), 8.34(d, 1 H, H_{10}, J(ortho) = 8 Hz), 7.72–7.36(m, 14 H, H_{12}–H_{11} and Ph).

4.4.5. Pd(nidf)Cl

Yellow; m.p.: 290–293 °C (dec.); yield, 90%. Anal. Found: C, 48.15; H, 4.34; N, 6.75. $C_{25}H_{19}ClN_3OPPd \cdot 4H_2O$ calc.: C, 48.25; H, 4.37; N, 6.75%. FT-IR cm^{-1}: ν(C–H)$_{arom.}$ = 3055$_w$, ν(C=C)$_{arom.}$ = 1608$_w$, ν(C=N) = 1578$_w$, ν(C–P) = 1436$_s$. ^{1}H NMR (CDCl$_3$, 25 °C) δ 9.35(s, 1 H, H_{13}), 8.65 (d, 1 H, CH=N, J(P–H) = 4 Hz), 8.47(t, 1 H, H_{11}, J(ortho) = 8 Hz), 8.45(sbr, 1 H, H_{12}), 8.43(d, 1 H, H_{10}, J(ortho) = 8 Hz), 7.73–7.29(m, 14 H, Ph).

4.4.6. Pd(inidf)Cl

Yellow, m.p.: 285–290 °C (dec.); yield, 80%. Anal. Found: C, 51.21, H, 3.98; N, 7.18. $C_{25}H_{19}ClN_3OPPd \cdot$

$2H_2O$ calc.: C, 51.22; H, 3.95; N, 7.17%. FT-IR cm^{-1}: ν(C–H)$_{arom.}$ = 3055$_{wbr}$, ν(C=C)$_{arom.}$ = 1617–1606$_w$, ν(C=N) = 1569$_w$, ν(C–P) = 1434$_s$. ^{1}H NMR (CDCl$_3$, 25°C): δ 8.67(sbr, 2 H, H$_{12}$–H$_{11}$), 8.44(d, 1 H, CH=N, J(P–H) = 4.1 Hz), 8.02(dbr, 2 H, H$_{13}$–H$_{10}$), 7.73–7.37(m, 14 H, Ph).

4.4.7. Pd(pidf)I

Brown; m.p.: 284–291°C (dec.); yield, 85.5%. Anal. Found: C, 46.75; H, 4.24; N, 6.59. C$_{25}$H$_{19}$IN$_3$OPPd calc.: C, 46.79; H, 2.98; N, 6.55%. FT-IR cm^{-1}: ν(C–H)$_{arom.}$ = 3044$_w$, ν(C=C)$_{arom.}$ = 1610$_w$, ν(C=N) = 1584$_w$, ν(C–P) = 1435$_m$. ^{1}H NMR (CDCl$_3$, 25°C): δ 8.65(d, 1 H, H$_{13}$, J(ortho) = 6 Hz), 8.54(d, 1 H, CH = N, J(P–H) = 4 Hz), 8.30(d, 1 H, H$_{10}$, J(ortho) = 8 Hz), 7.78–7.36(m, 16 H, Ph and H$_{12}$–H$_{11}$).

Orange crystals of formula Pd(pidf)I · $\frac{1}{4}$CH$_3$CN suitable for X-ray analysis were obtained by recrystallisation from a mixture CH$_2$Cl$_2$–CH$_3$CN (1:2 v:v).

4.4.8. Pd(nidf)I

Yellow-orange; m.p.: > 300°C; yield, 85%. Anal. Found: C, 46.70; H, 2.95; N, 6.58. C$_{25}$H$_{19}$IN$_3$OPPd calc.: C, 46.79; H, 2.98; N, 6.55%. FT-IR cm^{-1}: ν(C–H)$_{arom.}$ = 3055$_w$, ν(C=C)$_{arom.}$ = 1608$_w$, ν(C=N) = 1584$_w$, ν(C–P) = 1436$_m$. ^{1}H NMR (CDCl$_3$, 25°C): δ 9.33(d, 1 H, H$_{13}$, J(meta) = 1.5 Hz), 8.65(d, 1 H, H$_{12}$, J(ortho) = 7 Hz), 8.61(d, 1 H, CH=N, J(P–H) = 4 Hz), 8.51(t, 1 H, H$_{11}$, J(ortho) = 7 Hz), 8.34(d, 1 H, H$_{10}$, J(ortho) = 6 Hz), 7.77–7.18(m, 14 H, Ph).

4.4.9. Pd(inidf)I

Yellow-green; m.p.: 280–284°C (dec.); yield, 85%. Anal. Found: C, 46.79; H, 2.99; N, 6.49. C$_{25}$H$_{19}$IN$_3$OPPd calc.: C, 46.79; H, 2.98; N, 6.55%. FT-IR cm^{-1}: ν(C–H)$_{arom.}$ = 3056$_w$, ν(C=C)$_{arom.}$ = 1596$_w$, ν(C=N) = 1570$_w$, ν(C–P) = 1434$_m$. ^{1}H NMR (CDCl$_3$, 25°C): δ 8.64(d, 2 H, H$_{12}$–H$_{11}$, J(ortho) = 6 Hz), 8.33(d, 1 H, CH=N, J(P–H) = 4 Hz), 8.02(d, 1 H, H$_{13}$–H$_{10}$, J(ortho) = 6 Hz), 7.69–7.48(m, 14 H, Ph).

4.5. Synthesis of the complexes Pd(tsdf)Y (Y = CH$_3$CO$_2$, Cl, I)

A solution of the ligand (0.08 g, 0.220 mmol) in cold acetonitrile (40 ml) was slowly added to a solution containing an equimolar amount of palladium salt [Pd(CH$_3$CO$_2$) (0.049 g, 0.220 mmol) in acetonitrile (10 ml); K$_2$PdCl$_4$ (0.039 g, 0.220 mmol) in acetonitrile–water (25/15); K$_2$PdI$_4$ (0.079 g, 0.220 mmol) in acetone–water (30/20)]. The resultant mixture was stirred at room temperature for 3 h. After slow evaporation of the solvent, a microcrystalline product was filtered and washed with some little portion of Et$_2$O.

4.5.1. Pd(tsdf)(CH$_3$CO$_2$)

Orange; m.p.: 255–260°C (dec.); yield, 90%. Anal. Found: C, 49.99; H, 3.77; N, 7.96; S, 6.03. C$_{22}$H$_{20}$N$_3$O$_2$PPdS calc.: C, 50.06; H, 3.82; N, 7.76; S, 6.07%. FT-IR cm^{-1}: ν(NH$_2$)$_{asym.+sym.}$ = 3463$_{br}$–3352$_{br}$–3158$_{br}$, ν(C–H)$_{arom.}$ = 3055$_w$, ν(C=N) + δ(NH$_2$) = 1607$_m$, ν(CO$_2$)$_{asym.}$ = 1584$_{br}$, ν(C–P) = 1435$_s$, ν(CO$_2$)$_{sym.}$ = 1325$_s$, ν(C=S) = 1214$_w$, ν(C–S) = 748$_s$. ^{1}H NMR (CDCl$_3$, 25°C): δ 7.93(d, 1 H, CH=N, J(P–H) = 3 Hz), 7.70–7.00(m, 14 H, Ph), 5.17(s, 2 H, NH$_2$), 2.02(s, 3 H, CH$_3$CO$_2$); ^{31}P NMR (DMSO-d_6, 25°C): δ 23.30.

4.5.2. Pd(tsdf)Cl

Orange; m.p.: 286–292°C (dec.); yield, 80%. Anal. Found: C, 47.60, H, 3.39, N, 8.27, S, 6.35. C$_{20}$H$_{17}$ClN$_3$PPdS calc.: C, 47.64; H, 3.40; N, 8.33; S, 6.36%. FT-IR cm^{-1}: ν(NH$_2$)$_{asym.+sym.}$ = 3402$_w$–3280$_w$–3145$_w$, ν(C–H)$_{arom.}$ = 3055$_w$, ν(C=N) + δ(NH$_2$) = 1623$_s$, ν(C–P) = 1438$_m$, ν(C=S) = 1222$_w$, ν(C–S) = 748$_m$. ^{1}H NMR (CDCl$_3$, 25°C): δ 8.17(d, 1 H, CH=N, J(P–H) = 3.6 Hz), 7.66–7.30(m, 14 H, Ph), 5.12(s, 2 H, NH$_2$); ^{31}P NMR (DMSO-d_6, 25°C): δ 24.50.

4.5.3. Pd(tsdf)I

Orange; m.p.: 285–291°C (dec.); yield, 86%. Anal. Found: C, 40.38; H, 3.02; N, 6.97; S, 5.39. C$_{20}$H$_{17}$IN$_3$PPdS calc.: C, 40.32; H, 2.88; N, 7.05; S, 5.38%. FT-IR cm^{-1}: ν(NH$_2$)$_{asym.+sym.}$ = 3440$_w$–3287$_w$–3142$_w$, ν(C–H)$_{arom.}$ = 3052$_w$, ν(C=N) + δ(NH$_2$) = 1627$_m$, ν(C–P) = 1434$_m$, ν(C=S) = 1218$_w$, ν(C–S) = 748$_m$. ^{1}H NMR (CDCl$_3$, 25°C): δ 8.13(d, 1 H, CH=N, J(P–H) = 3 Hz), 7.64–7.25(m, 14 H, Ph), 5.15(s, 2 H, NH$_2$); ^{31}P NMR (DMSO-d_6, 25°C): δ 26.50.

4.6. Synthesis of the alkynyl complexes: Pd(pidf)(C = C–Ph), Pd(nidf)(C = C–Ph), Pd(inidf)(C = C–Ph), Pd(tsdf)(C = C–Ph)

A solution of the acetato complex [Pd(pidf)(CH$_3$CO$_2$), Pd(nidf)(CH$_3$CO$_2$), Pd(inidf)(CH$_3$CO$_2$) (0.05 g, 0.087 mmol) and Pd(tsdf)(CH$_3$CO$_2$) (0.05 g, 0.098 mmol)] in cold methanol (25 ml) was treated with an amount of phenylacetylene (1:10 molar ratio) [(0.091 g, 0.870 mmol) for Pd(pidf)(CH$_3$CO$_2$), Pd(nidf)(CH$_3$CO$_2$), Pd(inidf)(CH$_3$CO$_2$) and (0.102 g, 0.980 mmol) for Pd(tsdf)(CH$_3$CO$_2$)]. The resultant mixture was stirred at room temperature for 3 h. After slow evaporation of the solvent a microcrystalline product was isolated.

4.6.1. Pd(pidf)(C = C–Ph)

Yellow; m.p.: 245–248°C (dec.); yield, 60%. Anal. Found: C, 64.28; H, 4.00; N, 6.75. C$_{33}$H$_{24}$N$_3$OPPd

calc.: C, 64.35; H, 3.93; N, 6.82%. FT-IR cm^{-1}: ν(C–H)$_{arom.}$ = 3051$_w$, ν(C≡C) = 2117$_m$, ν(C=N) = 1593$_w$, ν(C–P) = 1436$_m$. ^{1}H NMR (CDCl$_3$, 25 °C): δ 8.73(d, 1 H, CH=N, J(P–H) = 3 Hz), 8.69(d, 1 H, H$_{13}$, J(ortho) = 5 Hz), 8.38(d, 1 H, H$_{10}$, J(ortho) = 8 Hz), 7.79–7.30(m, 16 H, Ph and H$_{12}$–H$_{11}$), 7.07(m, 3 H, para and meta to C≡C), 6.88(dd, 2 H, ortho to C≡C).

4.6.2. Pd(nidf)(C≡C–Ph)

Yellow, m.p.: 210–213 °C (dec.); yield, 35%. Anal. Found: C, 63.33; H, 4.00; N, 6.77. C$_{33}$H$_{24}$N$_3$OPPd calc.: C, 63.35; H, 3.93; N, 6.82%. FT-IR cm^{-1}: ν(C–H)$_{arom.}$ = 3055$_w$, ν(C≡C) = 2120$_m$, ν(C=C)$_{arom.}$ = 1600$_w$, ν(C=N) = 1584$_w$, ν(C–P) = 1435$_s$. ^{1}H NMR (DMSO-d_6, 25 °C): δ 9.50(s, 1 H, H$_{13}$), 8.99(d, 1 H, CH=N, J(P–H) = 4 Hz), 8.80 (dbr, 1 H, H$_{12}$), 8.74(tbr, 1 H, H$_{11}$), 8.70(d, 1 H, H$_{10}$, J(ortho) = 7 Hz), 8.25–7.20(m, 14 H, Ph), 7.15(m, 3 H, para and meta to C≡C), 6.99(dd, 2H, ortho to C≡C).

4.6.3. Pd(inidf)(C≡C–Ph)

Yellow; m.p.: 210–213 °C (dec.); yield, 55%. Anal. Found: C, 63.29; H, 3.98; N, 6.79. C$_{33}$H$_{24}$N$_3$OPPd calc.: C, 63.35; H, 3.93; N, 6.82%. FT-IR cm^{-1}: ν(C–H)$_{arom.}$ = 3053$_w$, ν(C≡C) = 2119$_m$, ν(C=C)$_{arom.}$ = 1594$_w$, ν(C=N) = 1568$_w$, ν(C–P) = 1434$_m$. ^{1}H NMR (CDCl$_3$, 25 °C): δ 8.66(d, 2 H, H$_{12}$–H$_{11}$, J(ortho) = 6 Hz), 8.52(d, 1 H, CH=N, J(P–H) = 2.5 Hz), 8.06(dd, 2 H, H$_{13}$–H$_{10}$, J(ortho) = 6 Hz, J(meta) = 1.5 Hz), 7.76–7.39(m, 14 H, Ph), 7.07(m, 3 H, para and meta to C≡C), 6.88(dd, 2 H, ortho to C≡C).

4.6.4. Pd(tsdf)(C≡C–Ph)

Brown, m.p.: 250–253 °C (dec.); yield, 75%. Anal. Found: C, 59.21; H, 3.85; N, 3.30; S, 5.61. C$_{28}$H$_{22}$N$_3$PPdS calc.: C, 59.01; H, 3.89; N, 3.37; S, 5.63%. FT-IR cm^{-1}: ν(NH$_2$)$_{asym.}$ = 3480$_{br}$, ν(NH$_2$)$_{sym.}$ = 3374$_{br}$, ν(C–H)$_{arom.}$ = 3055$_w$, ν(C≡C) = 2120$_w$, ν(C=N) + δ(NH$_2$) = 1597$_s$, ν(C–P) = 1437$_s$, ν(C=S) = 1212$_w$, ν(C–S) = 755$_s$. ^{1}H NMR (CDCl$_3$, 25 °C): δ 8.31(dbr, 1 H, CH=N), 7.79–7.14(m, 14 H, Ph), 7.04(m, 3 H, para and meta to C≡C), 6.75(dd, 2 H, ortho to C≡C), 5.27(s, 2 H, NH$_2$).

4.7. X-ray crystallography

Pertinent crystal data and basic information about the data collection and structure refinement are given in Table 7. The data were processed with the peak-profile analysis procedure and corrected for Lorentz-polarisation and absorption effects.

The structure was solved by a combination of direct methods and Fourier-difference techniques and refined by full-matrix least squares based on F^2. All non-hydrogen atoms were allowed anisotropic motion; the hydrogen atoms of the complex molecules were in-

Table 7
Summary of crystal data, intensity collection and refinement for Pd(pidf)I·$\frac{1}{4}$CH$_3$CN

Formula	C$_{25.5}$H$_{19.75}$IN$_{3.25}$OPPd
M	651.99
Crystal system	trigonal
Space group	$P3_121$
a /Å	13.065(5)
c /Å	49.15(1)
U /Å^3	7266(4)
Z	12
D_c /g cm^{-3}	1.788
Diffractometer	Cad 4 Enraf–Nonius
Radiation (λ /Å)	Mo Kα (0.71069)
μ /cm^{-1}	21.3
ϑ range/deg	3–30
Reflections measured	22300
Reflections unique	14166
Reflections observed [$F_o > 4\sigma(F_o)$]	6661
Parameters varied	593
$R1$ for observed data	0.0696
$wR2$ for all data	0.3446

cluded in idealised positions and refined riding on their carrier atoms, whereas those of the solvent molecule were ignored. Atomic scattering factors for neutral atoms were employed and the real and the imaginary parts of the anomalous dispersion effects were included in the structure factor calculations. Fractional atomic coordinates and equivalent isotropic thermal parameters are given in Table 8. Calculations were performed on Gould POWER NODE 6040 and ENCORE 91 computers using the program packages SIR92 [18], SHELXL93 [19], PARST [20] and ZORTEP [21].

4.8. Determination of the log β of the ligands

4.8.1. Spectrophotometric measurements

Each solution to be titrated was prepared in H$_2$O–methanol (80/20% v/v) (Hpidf, Hnidf, Hinidf) and H$_2$O–acetonitrile (50/50% v/v) (Htsdf) by subsequent addition of: (1) a weighted amount of the different ligands; (2) an exact volume of hydrochloric acid. Experimental measurements of pH were carried out with fully automatic apparatus equipped with Orion model 720A digital voltmeter and 5 ml Metrohm E665 motor burette, both controlled by a UVIKON 941 PLUS spectrophotometer guided by a personal computer. The electrodic chain consisted of a model OR (Orion Research) glass electrode (type 911SC) and a model OR reference electrode (type 9002). In the potentiometric vessel the solution was thermostated to 25.0 ± 0.1 °C and passed through the spectrophotometric cuvette using a peristaltic pump. The electrode system calibration was performed in terms of pH by using five fresh buffers (pH 2.0, 4.0, 7.0, 9.0, 11.0). After each addition of KOH (0.2 mol l^{-1}) solution the pH was measured and

Table 8

Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^4$) (one-third trace of the diagonalised matrix), with e.s.d.s in parentheses for Pd(pidf)I·$\frac{1}{4}$CH$_3$CN

Atom	x	y	z	U_{eq}
Pd1	3456.1(9)	−1891.3(9)	657.0(2)	399(4)
I1	4412.0(12)	−2107.4(10)	220.5(3)	725(7)
P1	4200.7(32)	24.3(30)	586.7(8)	404(15)
O1	2663(8)	−3676(8)	739(2)	421(43)
N1	2590(11)	−1989(10)	999(2)	420(54)
N2	1949(12)	−3136(10)	1109(3)	520(59)
N3	1680(12)	−5892(11)	950(3)	571(66)
C1	3750(13)	673(13)	862(3)	466(67)
C2	3076(13)	65(12)	1089(3)	428(62)
C3	2855(15)	706(15)	1283(3)	576(81)
C4	3212(17)	1876(16)	1255(4)	651(93)
C5	3832(20)	2448(17)	1037(5)	878(116)
C6	4106(19)	1882(15)	825(4)	710(103)
C7	2531(15)	−1193(15)	1143(3)	562(80)
C8	2057(12)	−3881(13)	957(3)	432(63)
C9	1356(11)	−5151(12)	1049(3)	405(56)
C10	392(15)	−5531(15)	1215(4)	627(86)
C11	−261(18)	−6735(15)	1278(4)	706(93)
C12	57(16)	−7499(14)	1172(4)	656(83)
C13	1040(17)	−7042(15)	1017(4)	621(88)
C14	3687(13)	395(12)	277(3)	460(64)
C15	2583(16)	276(16)	272(4)	709(100)
C16	2146(20)	492(19)	45(6)	892(129)
C17	2825(22)	871(17)	−180(4)	742(115)
C18	3933(21)	1037(18)	−186(5)	803(113)
C19	4359(17)	758(16)	44(4)	663(90)
C20	5813(13)	912(12)	586(3)	478(65)
C21	6412(14)	2044(15)	485(5)	687(88)
C22	7643(15)	2713(14)	490(4)	620(79)
C23	8255(15)	2249(17)	607(4)	629(84)
C24	7678(16)	1095(17)	705(5)	831(106)
C25	6469(15)	450(15)	699(4)	575(80)
Pd2	7782.1(9)	−1835.9(9)	936.1(2)	413(5)
I2	10018.7(9)	−475.0(10)	863.6(3)	663(5)
P2	7732.4(31)	−3383.0(30)	747.4(8)	401(15)
O2	7620(9)	−649(9)	1188(2)	497(46)
N4	6002(9)	−2687(11)	982(3)	454(54)
N5	5639(11)	−2093(11)	1167(3)	477(59)
N6	7122(12)	635(11)	1524(3)	546(63)
C26	6306(13)	−4329(12)	574(3)	421(64)
C27	5286(12)	−4356(12)	664(3)	400(59)
C28	4213(13)	−5186(14)	549(3)	494(71)
C29	4164(13)	−5968(14)	349(4)	575(73)
C30	5194(15)	−5901(15)	260(3)	555(81)
C31	6253(13)	−5082(13)	379(3)	480(68)
C32	5185(12)	−3570(13)	868(3)	477(64)
C33	6539(12)	−1080(12)	1254(3)	414(62)
C34	6211(12)	−379(12)	1435(3)	399(60)
C35	5056(15)	−800(16)	1522(4)	650(88)
C36	4839(19)	−76(19)	1683(4)	750(118)
C37	5747(19)	953(17)	1776(4)	726(105)
C38	6866(16)	1268(14)	1696(4)	573(79)
C39	7760(12)	−4286(13)	1019(4)	463(66)
C40	8446(15)	−3762(15)	1250(3)	558(79)
C41	8372(15)	−4433(16)	1478(4)	590(86)
C42	7684(17)	−5621(16)	1475(5)	779(104)
C43	7046(21)	−6171(17)	1250(5)	953(126)
C44	7072(17)	−5498(15)	1028(4)	742(92)
C45	8819(12)	−3215(13)	498(3)	465(66)
C46	8882(14)	−2631(15)	258(4)	589(80)

Table 8 (continued)

Atom	x	y	z	U_{eq}
C47	9731(19)	−2433(17)	68(4)	744(106)
C48	10570(19)	−2711(19)	113(5)	813(111)
C49	10545(15)	−3288(19)	356(5)	801(110)
C50	9685(13)	−3513(14)	547(4)	549(76)
C51	0	419(22)	1667	972(183)
C52	0	−684(27)	1667	799(140)
N7	0	−1559(24)	1667	1074(176)

the absorbance data in the range 230–430 nm were collected and recorded. The range of concentration of various ligands in the spectrophotometric titration was 2.2835×10^{-5} to 8.1882×10^{-5} mol l^{-1}.

4.8.2. Calculations

All the protonation constants for the different ligands have been obtained through the refinement of several sets of measurements of absorption data with the computer program SQUAD [22]. Typically the data contain the absorbance values A_s for a certain number of wavelengths in each one of a certain number of equilibrium solutions of known analytical composition (pH and c_L). Assuming that Beer's law is valid, we know that for each solution and wavelength the absorbance A_s is defined by the equation

$$A_{c,ik} = l \sum_0^p \sum_0^q \beta_{p,q}[L]^p[H]^q \varepsilon_{p,q}$$

(where ε_{pq} is the molar extinction coefficient for the species $[H_qL_p]$ and l is the pathlength of the cuvette used), the sum being extended over all the free and protonated species which are assumed to be present in solution. The unknown parameters in this equation are: [L] (free ligand ion concentration) for each solution, ε_{pq} at all wavelengths and β_{pq} (protonation constant). The values of [H] are obtained from potentiometric measurements. The program SQUAD calculates the values of the cumulative protonation constants which minimise the weighted sum U of the squared residual between observed and calculated absorbance values as previously described.

4.9. General procedure for the catalytic hydrogenation of styrene and phenylacetylene

All manipulations were carried out under purified dry nitrogen by use of standard Schlenk techniques. The solvent was dried and stored under nitrogen. A 50 ml round-bottomed flask with a lateral arm with a stopcock and a top equipped for gas chromatographic sampling and magnetic stirrer, was fitted to a hydrogenation apparatus consisting of a 1 l burette and a reservoir filled with an NaCl–H$_2$O solution. The unsaturated

substrates and the complex (100:1 molar ratio) were dissolved in methanol in the hydrogenation flask in order to have a homogeneous solution and thermostated to 25 °C. The concentration of the catalyst was 1.363×10^{-3} mol l^{-1}. The progress of the reaction was followed by gas chromatography (GC).

At the end of the reaction, Et$_2$O was added to favour the complete precipitation of the complex, which was filtered off.

4.9.1. Hydrogenation of styrene

The experimental conditions for the complexes of the ligand Hinidf are as follows:

(a) 0.015 g of Pd(inidf)(CH$_3$CO$_2$) (0.026 mmol, entry 4 in Table 4) were dissolved in 19 ml of dry methanol; 0.27 g of styrene (2.614 mmol) were added to the solution that was thermostated to 25 °C. After 18 h of reaction styrene was quantitatively converted to ethylbenzene and the starting complex was completely recovered.

(b) 0.014 g of Pd(inidf)Cl (0.026 mmol, entry 9 in Table 4) were dissolved in 19 ml of dry methanol; 0.26 g of styrene (2.544 mmol) were added to the solution that was thermostated to 25 °C. After 48 h of reaction styrene was converted to ethylbenzene (0.013 g, 0.123 mmol) in 5% yield and the starting complex was completely recovered.

(c) 0.017 g of Pd(inidf)I (0.026 mmol) were dissolved in 19 ml of dry methanol; 0.27 g of styrene (2.590 mmol) were added to the solution that was thermostated to 25 °C. After 48 h of reaction styrene was converted to ethylbenzene (0.005 g, 0.051 mmol) in 2% yield and the starting complex was completely recovered.

4.9.2. Hydrogenation of phenylacetylene

The experimental conditions for the complexes of the ligand Hinidf are as follows:

(a) 0.015 g of Pd(inidf)(CH$_3$CO$_2$) (0.026 mmol, entry 4 in Table 5) were dissolved in 19 ml of dry methanol; 0.27 g of phenylacetylene (2.614 mmol) were added to the solution that was thermostated to 25 °C. After 18 h of reaction phenylacetylene was converted to styrene (0.146 g, 1.402 mmol) in 54% yield and to ethylbenzene (0.124 g, 1.172 mmol) in 46% yield. For evaporation of the solvent a yellow solid of formula Pd(inidf)(C≡C–Ph) was recovered.

(b) 0.014 g of Pd(inidf)Cl (0.026 mmol, entry 10 in Table 5) were dissolved in 19 ml of dry methanol; 0.26 g of phenylacetylene (2.544 mmol) were added to the solution that was thermostated to 25 °C. After 24 h of reaction phenylacetylene was converted to styrene (0.239 g, 2.300 mmol) in 92% yield and to ethylbenzene (0.021 g, 0.196 mmol) in 8% yield. The starting complex was completely recovered.

(c) 0.017 g of Pd(inidf)I (0.026 mmol) were dissolved in 19 ml of dry methanol; 0.27 g of phenylacetylene

(2.649 mmol) were added to the solution that was thermostated to 25 °C. After 48 h of reaction phenylacetylene was converted to styrene (0.032 g, 0.312 mmol) in 12% yield; no ethylbenzene was determined.

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