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Note

Protonation of palladium(II)-allyl and palladium(0)-olefin complexes containing 2-pyridyldiphenylphosphine

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ABSTRACT

The pendant nitrogen atom of the Ph_2PPy ligand in the Pd(II)-allyl complexes [PdCl(η^3-2-CH_3-C_3H_4)(Ph_2PPy)] (**1**) and [Pd(η^3-2-CH_3-C_3H_4)(Ph_2PPy)$_2$]BF_4 (**3**) has been protonated with methanesulfonic acid to afford the corresponding pyridinium salts [PdCl(η^3-2-CH_3-C_3H_4)(Ph_2PPyH)](CH_3SO_3) (**1a**) and [Pd(η^3-2-CH_3-C_3H_4)(Ph_2PPyH)$_2$](CH_3SO_3)$_2$(BF_4) (**3a**).

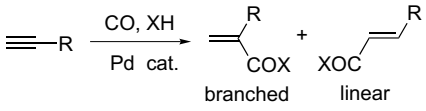
Protonation strongly influences the ^1H and ^{13}C NMR spectral parameters of the allyl moieties of **1a** and **3a** whose signals resonate at lower fields with respect to the parent species indicating that upon protonation Ph_2PPy becomes a weaker σ-donor and a stronger *Π*-acceptor. The allyl moiety, which in **1** is static, becomes dynamic in **1a**, the observed *syn–syn* and *anti–anti* exchange being due to deligation of the protonated phosphine from the metal centre. Treatment of complex **3** with diethylamine in the presence of fumaronitrile gives the new Pd(0)-olefin complex [Pd(η^2-fumaronitrile)(PPh_2Py)$_2$] (**4**) which has been characterized by elemental analysis and NMR spectroscopy. Low temperature protonation of **4** with methanesulfonic acid leads to the bis-protonated species [Pd(η^2-fumaronitrile)(Ph_2PPyH)$_2$](CH_3SO_3)$_2$ (**4a**) which is stable only at temperatures <0 °C.

1. Introduction

The transition-metal catalyzed carbonylation of alkynes is an important synthetic tool in the synthesis of intermediates and fine chemicals [1–3]. Among the catalysts which promote the reaction, the system formed by $Pd(OAc)_2$ in combination with 2-pyridyldiphenylphosphine (Ph_2PPy) and methanesulfonic acid is of particular interest since it provides very high activities accompanied by almost complete chemoselectivity (no saturated product arising from double carbonylation is formed) and regioselectivity (the branched to linear isomer ratio is about 200:1) (Scheme 1) [4].

Even if it has been firmly established that the use of Ph_2PPy as the ligand in combination with a strong protic acid as the promoter is essential to achieve high reaction rates [2,4], the mechanism of the reaction and the reasons for the excellent selectivity are still unclear, in particular as far as the role of the ligand and the acid is concerned [5,6].

It has been suggested that the very high reaction rate observed using Ph_2PPy is to attribute to the double role that this ligand might play in catalysis, in fact: (i) since it is a P donor ligand it contributes to stabilize the catalytically active species, and (ii) it provides a pendant nitrogen atom which could assist the transport of the protons from the core of the reaction medium into the coordination sphere of the metal [4,5]. The importance of bifunctional organometallic catalysts containing basic sites in proton transfer processes has been recently reviewed by Grotjahn [7].



Pd cat. : $Pd(OAc)_2/Ph_2PPy/CH_3SO_3H$
R = alkyl, aryl
X = OH, OR', NR'_2 ; branched:linear ~ 200:1

Scheme 1. Synthetic utility of the alkyne carbonylation.

The chemistry of Ph_2PPy has been the subject of a large number of investigations [8,9]. Faraone and co-workers have shown that the pyridyl nitrogen atom of a P-bonded Ph_2PPy can be protonated by HPF_6 [10]. However, to the best of our knowledge, there are no studies dealing with the effects brought about by protonation on the coordination ability of Ph_2PPy.

Prompted by our interest in the use of this catalytic system in fine chemistry [11] and in the mechanism of the reaction [5], we have investigated the NMR behavior of some palladium allyl complexes containing Ph_2PPy in the presence of methanesulfonic acid.

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We were confident that the allyl moiety could withstand the presence of a strong protic acid [12] and behave as a reporter ligand able to highlight the modifications caused by protonation on the electronic properties of the phosphine and the metal centre. For instance, it is well-know that the dynamic behavior of Pd-allyl complexes is strongly affected by the electronic and steric properties of the ancillary ligands [12,13]. In this connection, it is worth of note that the reports dealing with palladium allyl complexes containing Ph_2PPy are rare [6a,9,14,15]. We employed palladium allyl complexes in our investigations also because they are convenient starting compounds for the synthesis of Pd(0)-alkene species *via* reductive amination [6a,16–19]; accordingly we report herein details on the synthesis of the new Pd(0) complex [Pd(η^2-fumaronitrile)($Ph_2PPy)_2$] and on its protonation.

2. Results and discussion

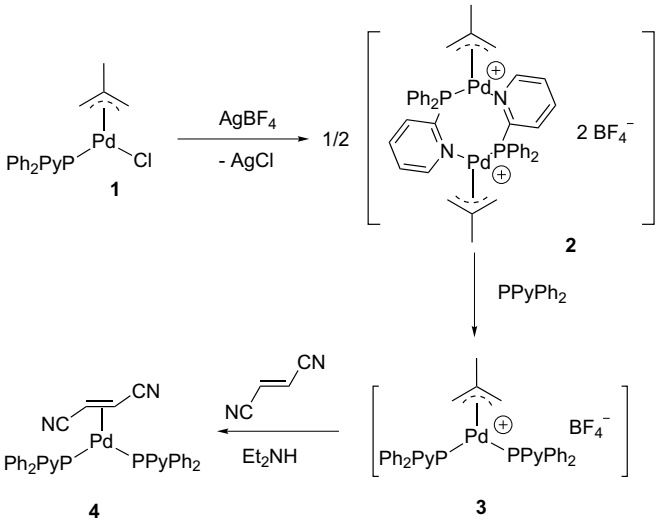
2.1. Synthesis and characterization of the palladium complexes

The complexes **1** [10,14], **2** [15] and **3** [15] were prepared according to the literature as outlined in Scheme 2. The hitherto unreported Pd(0)-olefin complex **4** was obtained in good yield by treating complex **3** with three equivalents of diethylamine in the presence of fumaronitrile according to a well-know method for the synthesis of zerovalent palladium olefin complexes [16,17].

Complex **4** was characterized by elemental analysis and multinuclear NMR spectroscopy. As usual for this type of complexes in the ^1H NMR spectrum the protons of the coordinated fumaronitrile appear as the AA′ part of an AA′XX′ multiplet centered at δ 3.19 [17–19] which integrates in the correct ratio with the Ph_2PPy protons (partially overlapping multiplets at δ 7.1–7.5 and a doublet at δ 8.54). Owing to the chemical equivalence of the phosphorus atoms of the ligands, the $^{31}P\{^1H\}$ NMR spectrum of **4** consists of a singlet at δ 27.6. In the $^{13}C\{^1H\}$ NMR spectrum the resonance of the olefin carbons appears as the A part of a AXX′ spin system (the X nuclei are the two phosphorus atoms of Ph_2PPy) centered at δ 33.7 in keeping with the literature data for similar Pd(0)-fumaronitrile complexes [20,21].

It is noteworthy that in the $^{13}C\{^1H\}$ NMR there are two well separate sets of resonances for the carbon atoms of the phenyl rings according to the different spatial position they occupy with respect to the Pd-fumaronitrile moiety. Furthermore, it is to point out that the resonances of the *ipso*-, *ortho*- and *meta*- carbon atoms of the aromatic rings are AXX′ multiplets providing evidence that the ligands are firmly coordinated to palladium.

Other examples of palladium(0) complexes containing Ph_2PPy and alkenes or alkynes bearing electron-withdrawing substituents have been previously reported by Edwards and co-workers [6a].



Scheme 2. Synthesis of the palladium complexes used in protonation studies.

2.2. Protonation of 2-pyridyldiphenylphosphine

As preliminary investigation, we have fully assigned the ^1H and $^{13}C\{^1H\}$ NMR spectra of the free phosphine by means of 2D NMR. The data for the hydrogen and carbon atoms of the pyridyl moiety are reported in Table 1 (the relevant numbering scheme is shown in Fig. 1); the chemical shifts of ^{13}C resonances of the phenyl rings are reported in Section 4.

Addition of one equivalent of methanesulfonic acid to a dichloromethane solution of 2-pyridyldiphenylphosphine followed by dilution with diethyl ether affords the corresponding pyridinium salt in almost quantitative yield. As observed for pyridine [22], upon protonation the resonances of all the hydrogen atoms belonging to the pyridyl moiety move to lower fields. The differences in the chemical shifts $\Delta\delta$ ($\Delta\delta = \delta_{protonated} - \delta_{unprotonated}$) are in the order: $\Delta\delta$(H-4Py) $\approx \Delta\delta$(H-5Py) > $\Delta\delta$(H-6Py) > $\Delta\delta$(H-3Py) (see Table 1) in keeping with the behavior found for pyridine [23]. In addition, it appears that also the resonances of the phenyl ring protons are displaced to lower fields even if the single $\Delta\delta$ values were not evaluated. At room temperature in CD_2Cl_2 the N–H of the pyridinium salt is a very broad featureless singlet centered at ca. 14.0 δ. On lowering the temperature at 195 K, the slow exchange temperature region is reached and the signal sharpens giving rise to an apparent triplet since $J_{H\text{-}6Py\text{–}H\text{-}5Py} \approx J_{H\text{-}6Py\text{–}NH}$.

In the $^{13}C\{^1H\}$ NMR upon protonation the C-2Py and C-6Py resonances move to higher fields in contrast with the C-3Py, C-4Py and C-5Py resonances which are shifted to lower fields similarly to what found for pyridine [23]. Upon protonation also all the resonances of the carbon atoms belonging to the phenyl rings are shifted to lower fields, the effect is in the order $\Delta\delta$(C1-Ph) (+3.2 ppm) $\gg \Delta\delta$(C3-Ph) (+0.9 ppm) $\approx \Delta\delta$(C4-Ph) (+0.7 ppm) > $\Delta\delta$(C2-Ph) (+0.2 ppm). In the $^{31}P\{^1H\}$ NMR, addition of methanesulfonic acid to 2-pyridyldiphenylphosphine displaces the resonance of the phosphorus atom to higher fields (free ligand: δ = −3.5, protonated ligand: δ = −6.5).

2.3. Protonation of complex *1*

The protonations of complexes **1**–**4** were carried out *in situ* by adding aliquots of methanesulfonic acid (up to an acid:phosphorus molar ratio of 1:1) to NMR tubes containing 0.05–0.02 M solutions of the palladium complexes in CD_2Cl_2.

Addition of one equivalent of acid to complex **1** leads to the corresponding pyridinium salt **1a**. In fact, all the proton resonances of the pyridyl moiety are shifted downfield in almost the same way as in the protonation of the free ligand (see Table 1). The differences in the chemical shifts $\Delta\delta$ are in the order: $\Delta\delta$(H-4Py) $\approx \Delta\delta$(H-5Py) > $\Delta\delta$(H-6Py) > $\Delta\delta$(H-3Py) in keeping with the behavior found for pyridine and the free ligand.

In the $^{13}C\{^1H\}$ NMR spectrum, upon protonation the C-2Py and C-6Py resonances are displaced to higher fields while the signals of C-3Py, C-4Py and C-5Py move downfield (Table 1) again similarly to that observed for pyridine and 2-pyridyldiphenylphosphine.

The allyl moiety, which in complex **1** is rigid, upon protonation becomes dynamic [24], as indicated by the broad profiles of the relevant proton resonances. On lowering the temperature, the allyl resonances of **1a** sharpen and a static spectrum is obtained at 253 K. 2D NMR experiments allow the definite assignment of the low temperature spectrum as reported in Table 2 (for the numbering system see Fig. 1).

Table 1
Selected ^{1}H and ^{13}C NMR data for the protonation of complexes **1–4** and Ph_2PPy.[a]

	δ(H-3Py) [Δδ]	δ(H-4Py) [Δδ]	δ(H-5Py) [Δδ]	δ(H-6Py) [Δδ]	δ(C-2Py) [Δδ]	δ(C-3Py) [Δδ]	δ(C-4Py) [Δδ]	δ(C-5Py) [Δδ]	δ(C-6Py) [Δδ]
Ph_2PPy	7.15	7.60	7.22	8.72	164.0	128.2	135.9	122.5[b]	150.5
Ph_2PPyH^+	7.27 [+0.12]	8.22 [+0.62]	7.82 [+0.60]	9.16 [+0.44]	160.1 [−3.9]	130.9 [+2.7]	144.5 [+8.6]	125.9 [+3.4]	145.0 [−5.5]
1	7.4[b]	7.7[b]	7.33	8.76	157.7[c]	130.0[c]	135.9[c]	123.8[c]	150.2[c]
1a	7.7[b,d] [∼+0.3]	8.32[d] [∼+0.6]	7.96[d] [+0.63]	9.24[d] [+0.48]	153.4[c] [−4.3]	131.4[c] [+1.4]	143.4[c] [+7.5]	127.0[c] [+3.2]	146.0[c] [−4.2]
3	7.06	7.45	7.20	8.44	156.9	128.0	136.6	124.8	150.6
3a	7.6[b] [∼+0.5]	8.17 [+0.72]	7.8[b] [∼+0.6]	8.32 [−0.12]	152.3 [−4.6]	∼129.8[e] [∼+1.8]	142.6 [+6.0]	127.1 [+2.3]	147.4 [−3.2]
4	7.1[b]	7.5[b]	7.2[b]	8.54	159.7	∼128.3[e]	135.8	123.5	150.4
4a	7.5[b,d] [∼+0.4]	8.11[d] [∼+0.6]	7.67[d] [∼+0.5]	8.61[d] [+0.07]	151.9[f] [−7.8]	129.9[f] [∼+1.6]	145.3[f] [+9.5]	127.4[f] [+3.9]	145.5[f] [−4.9]

[a] Spectra registered on CD_2Cl_2 solutions (0.01–0.04 M) at 298 K unless otherwise stated, $\Delta\delta = \delta_{protonated} - \delta_{unprotonated}$.
[b] Resonance obscured by the phenyl protons and detected by COSY NMR.
[c] Spectrum registered in $CDCl_3$ at 298 K.
[d] Spectrum registered in CD_2Cl_2 at 253 K.
[e] Resonance obscured by phenyl carbons.
[f] Spectrum registered in CD_2Cl_2 at 233 K.

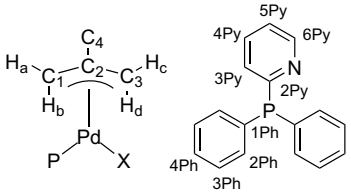


Fig. 1. Numbering scheme for Ph_2PPy and the allyl moiety.

By comparing the data of parent complex **1** and those of **1a** it appears that all the resonances of allyl protons move to lower fields upon protonation indicating that σ-donor ability of 2-pyridyldiphenylphosphine decreases upon protonation.

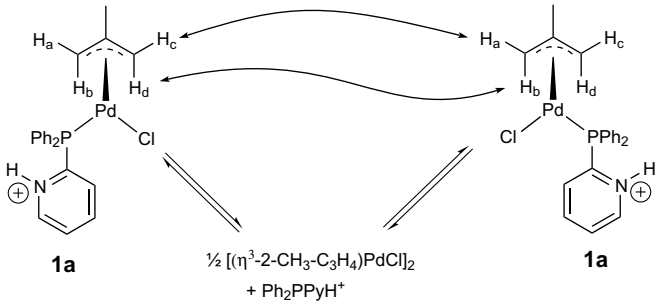
It is worthy of note that the allyl protons on the carbon atom *cis* to protonated Ph_2PPy are more deshielded than the *trans* ones. A similar effect has been previously described by Pörschke et al. [25] who noticed that in a homologous series of $[Pd(allyl)(PR_3)X]$ complexes on decreasing the donor ability of the X group, the allyl resonances are displaced to lower fields the effect being larger for the allyl protons in *cis* to the X group.

In the $^{13}C\{^{1}H\}$ NMR spectrum all the resonances of the allyl carbons of **1a** appear deshielded with respect to the parent complex **1**; it is interesting to note that the effect is larger for the carbon atom *trans* to the phosphine and the central carbon atom in contrast with that found for the proton resonances.

It should be noted that in complex **1a** the N–H and the Pd–Cl moieties are close together so that the existence of an intramolecular N–H···Cl hydrogen bonding interaction cannot be ruled out; such interaction should decrease the σ-donor ability of the chloride and hence also affect to some extent the chemical shifts of the allyl group.

Most importantly, the reduced σ-donor ability of Ph_2PPyH^+ is decisive in determining the dynamic behavior of **1a** observed at room temperature. As a matter of fact, ^{1}H NMR spin saturation transfer experiments [26] show that the allyl dynamic is to be attributed to a *syn–syn*, *anti–anti* exchange. The experiments were carried out at 273 K since at this temperature the exchange is quite slow and the ^{1}H NMR spectrum displays four separate broad resonances for the terminal allyl protons. Selective irradiation of the H_a resonance at δ 3.42 causes a strong decrease of the intensity of the H_c signal at δ 4.64 and the same behavior is observed for the H_b–H_d proton pair. Such *syn–syn* and *anti–anti* exchange can be accounted for by assuming reversible dissociation of the protonated ligand as shown in Scheme 3.

This hypothesis on the nature of the dynamic process is definitively assessed by the results of two dimensional ^{31}P–^{1}H NMR correlation experiments which definitely show that at room temperature the protonated phosphine dissociates from the metal centre.



Scheme 3. Dynamic behavior of complex **1a**.

Table 2
NMR data for the allyl and the olefin moieties of complexes **1–4**.[a]

Complex	δ(CH_3) [Δδ]	δ(H_b) [Δδ]	δ(H_a) [Δδ]	δ(H_d) [Δδ]	δ(CH) [Δδ]	δ(H_c) [Δδ]	δ(C_1) [Δδ]	δ(C_2) [Δδ]	δ(C_3) [Δδ]	δ(C_4) [Δδ]	δ(=C) [Δδ]
1	1.96	2.76	3.06	3.56		4.48	61.3[b]	132.9[b]	78.0[b]	23.2[b]	
1a	2.03[c]	3.08[c]	3.43[c]	3.70[c]		4.62[c]	62.3[b]	134.6[b]	79.6[b]	23.2[b]	
	[+0.07]	[+0.32]	[+0.37]	[+0.14]		[+0.14]	[+1.0]	[+1.7]	[+1.6]	[0]	
3	1.89	3.21	3.82	3.21		3.82	76.9	138.2	76.9	23.4	
3a	1.97	3.90	3.93	3.90		3.93	80.6	140.0	80.6	23.2	
	[+0.9]	[+0.69]	[+0.11]	[+0.69]		[+0.11]	[+3.7]	[+1.8]	[+3.7]	[−0.2]	
4					3.19						33.7
4a					3.53[c]						36.5[d]
					[+0.34]						[+2.8]

[a] In CD_2Cl_2 at 298 K unless otherwise stated.
[b] In $CDCl_3$ at 298 K.
[c] In CD_2Cl_2 at 253 K.
[d] In CD_2Cl_2 at 233 K.

The ^{31}P NMR spectrum of **1** consists of a singlet at δ 26.0 [15] which moves downfield to δ 26.8 upon protonation; it is worth noting that the $\Delta\delta$ (+0.8, at 253 K) is much smaller and opposite in sign to that observed in the protonation of the free ligand ($\Delta\delta = -3.0$).

2.4. Protonation of complex *2*

The dinuclear complex **2** was treated with methanesulfonic acid to ascertain whether addition of a proton could break the palladium–nitrogen bond and open the ring structure, but no protonation is observed even if complex **2** is treated with two equivalent of methanesulfonic acid at room temperature. Moreover, when **2** is treated with a large excess of acid (four equivalents) decomposition to ill-defined products occurs within 24–36 h.

2.5. Protonation of complex *3*

In spite of its cationic nature, complex **3** promptly reacts with two equivalents of methanesulfonic acid to give the protonated derivative **3a** (Scheme 4).

Protonation of both pyridyl moieties is supported by the observation that in the ^{1}H and $^{31}P\{^{1}H\}$ NMR spectra of **3a**, registered over a wide temperature range (from +25 to −85 °C), the two ligands appear chemically equivalent.

As observed for the free phosphine and complex **1**, upon protonation the resonances of protons H-3Py, H-4Py and H-5Py move to lower fields and the difference in the chemical shifts are in the order $\Delta\delta$(H-4Py) ≈ $\Delta\delta$(H-5Py) > $\Delta\delta$(H-3Py); quite surprisingly, in **3a** the H-6Py resonance is displaced upfield ($\Delta\delta = -0.12$ ppm) (see Table 1). Although we have no rationale for this finding, we tentatively attribute this odd behavior to solvent effects; indeed, it should be pointed out that in the $^{13}C\{^{1}H\}$ NMR spectrum the C-3Py, C-4Py and C-5Py resonances move to low fields and the C-6Py and C-2Py signals shift to higher fields similarly to that found for **1a** and Ph_2PPyH^+. It is interesting to note that some of the aromatic carbon resonances (see Section 4) display strong second order character being coupled with two chemically, but not magnetically equivalent phosphorus atoms.

In keeping with the chemical equivalence of the two phosphorus atoms the $^{31}P\{^{1}H\}$ NMR spectrum of **3a** consists of a singlet at δ 26.6. It is noteworthy that the $\Delta\delta$ value (+0.2) is much smaller than that observed for the protonation of **1** and opposite in sign to that observed for the protonation of the free phosphine.

As far as the allyl moiety is concerned, upon protonation the *anti* protons (an AA′XX′ multiplet) undergo a considerable displacement to lower fields: from δ 3.21 (complex **3**) to δ 3.90 (complex **3a**), $\Delta\delta = 0.69$; the *syn* protons (singlet) also move to lower field ($\Delta\delta = 0.12$), so that in **3a** the resonances of the *syn* and the *anti* protons almost coincide (Table 2).

In the $^{13}C\{^{1}H\}$ NMR spectrum the two terminal carbon atoms of the allyl moiety are chemically but not magnetically equivalent and give rise to an AA′X resonance centered at δ 80.6, while the central carbon resonance is a triplet at δ 140.0 as found for the parent complex **3** [15]. These data show that also the allyl carbon atoms of **3a** are significantly deshielded upon protonation. It is to point out that the $\Delta\delta$ of the terminal carbons is much larger than that of the central carbon atoms (see Table 2) and that the overall effect is larger than that observed in the protonation of complex **1**.

The influence of the nature of the ligands on the ^{13}C NMR spectra of a series of symmetrically substituted complexes of formulation $[Pd(\eta^3\text{-}2\text{-}CH_3\text{-}C_3H_4)L_2] + (L = Cl^-$, amine, phosphine or L_2 = 1,5-cyclooctadiene) has been studied by Åkermark [27] who concluded that the resonances of the terminal carbon atoms undergo significant downfield displacements when the L ligands have *Π*-acceptor character; accordingly, the above results suggest that upon protonation not only Ph_2PPy becomes a weaker σ-donor, but also increases its *Π*-acceptor ability.

No dynamic behavior was detected for **3a**. Indeed, even if upon protonation at room temperature the resonances of the two type of allylic protons become very close, they retain their own profiles so that a *syn–anti* exchange of the allyl hydrogen atoms can be ruled out; moreover, in the ^{1}H and ^{13}C NMR spectra of **3a** all the resonances relevant to the allyl moiety couple with the phosphorus atoms of Ph_2PPyH^+, ruling out dissociation of the protonated ligand.

2.6. Protonation of complex *4*

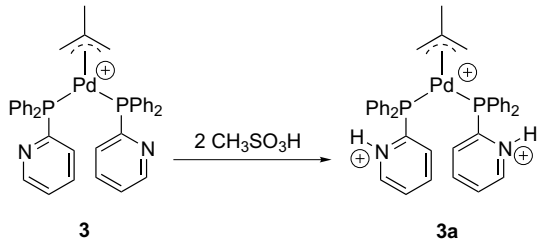
Treatment of complex **4** with two equivalents of methanesulfonic acid at −70 °C leads to the formation of the protonated complex **4a** (Scheme 5).

As it will be discussed below, **4a** is not stable under ambient conditions and it has been characterized by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy at low temperature. Protonation occurs on both pyridyl moieties as inferred from the observation that in the NMR spectra both ligands appear chemically equivalent. In the ^{1}H NMR spectrum of **4a** all the pyridyl signals resonate at fields lower than in the non-protonated parent compound, the greatest $\Delta\delta$ values being observed for H-4Py and for H-5Py (see Table 1). In the $^{13}C\{^{1}H\}$ NMR spectrum (recorded at 233 K) the resonances of C-3Py, C-4Py and C-5Py move to lower fields and at the same time C-2Py, C-6Py are displaced to higher fields as found for Ph_2PPy, **1** and **3** (see Table 1). Moreover, as for **4**, two different sets of signals are detected for the phenyl rings of coordinated Ph_2PPyH^+.

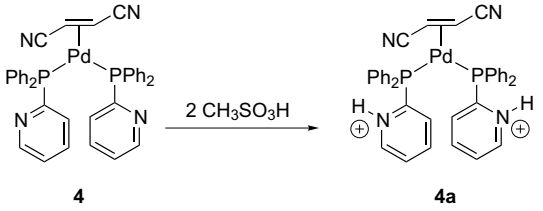
The fumaronitrile protons of **4a** appear as an AA′XX′ multiplet centered at δ 3.53, about 0.4 δ downfield of the corresponding signal in **4**, indicating a significant decrease of the electron density at the metal centre. Reduction of the electron density at the metal centre is confirmed by the shift to lower fields of the resonance of the olefin carbon atoms (AXX′ multiplet at 36.5 δ, $\Delta\delta = +2.8$, see Table 2). Hence, these data further highlight the weak σ-donor ability of $Ph_2PPyH^+$and its improved *Π*-acceptor character.

Finally, it is to mention that the ^{31}P NMR of **4a** consists of a singlet at δ 26.4, thus it appears that, at variance with that found for complexes **1a** and **3a**, the signal moves to lower fields ($\Delta\delta = -0.2$) on protonation.

As anticipated, **4a** is not thermally stable and slowly decomposes on standing at temperatures above 0 °C. The process is slow



Scheme 4. Protonation of complex **3**.



Scheme 5. Protonation of complex **4**.

even at room temperature and in the early stages consists of a "clean" deligation of the olefin from the metal centre which can be monitored recording the growth of the singlet due to uncoordinated fumaronitrile at δ 6.35 in the ^{1}H NMR spectrum. Experiments aimed to highlight the fate of the metal fragment were unsuccessful and in particular it should be mentioned that no evidence supporting the formation of palladium-hydride species [21,28] was found. On standing the solutions of **4a** darken, thus, it is likely that at the end the decomposition leads to colloidal palladium.

The poor stability of **4a** is likely to be attributed to the reduced σ-donor ability of Ph_2PPyH^+ and its improved *Π*-acceptor character: since *Π*-back-donation from the metal is a key factor in determining the stability of the fumaronitrile–palladium bond [17,19,29], it is conceivable that ligand protonation leads to a significant decrease of the electron density at the metal centre so that the back-donation from the metal to the olefin decreases and the palladium–fumaronitrile interaction is substantially weakened.

3. Conclusions

This study shows that the palladium allyl moiety is quite robust and able to withstand the treatment with strong protic acids such as the methanesulfonic acid. Thus, complexes **1** and **3** containing the P monodentate 2-pyridyldiphenylphosphine are smoothly protonated at the pendant nitrogen atom forming the corresponding species containing the 2-(diphenylphosphino)pyridinium ion acting as a P monodentate ligand; these complexes appear stable even under ordinary atmosphere at room temperature. The effects brought about by the protonation on the ^{1}H and ^{13}C NMR resonances of the allyl moieties of both **1** and **3** indicate that the protonated phosphine is a poor σ-donor and an enhanced *Π*-acceptor. The scarce donor ability of the 2-(diphenylphosphino)pyridinium ligand is confirmed by the thermal unstability of complex **4a**. Finally, it should be remarked that the deligation of fumaronitrile from the metal centre suggests a rationale for the complete chemoselectivity observed in the catalytic alkyne carbonylation: a second carbonylation does not occur probably because the formed acrylic acid derivative is unable to coordinate to palladium.

4. Experimental

^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectra were registered on a Bruker Avance 300 spectrometer operating at 300.213, 75.44, and 100.015 MHz, respectively. ^{1}H and ^{13}C chemical shifts are reported relative to TMS using solvent resonances as a secondary reference. ^{31}P chemical shifts are reported relative to external 85% H_3PO_4. All manipulations were performed under argon atmosphere using standard Schlenk techniques. Solvents (Aldrich) were purified according to standard literature methods [30].

Fumaronitrile and methanesulfonic acid were high purity commercial products (Aldrich) and were used as received. Commercial Ph_2PPy (Aldrich) was recrystallized from methanol. [Pd(η^3-2-CH_3-C_3H_4)Cl]$_2$ [31], [PdCl(η^3-2-CH_3-C_3H_4)(Ph_2PPy)] [9,14], [Pd_2(η^3-2-CH_3-C_3H_4)$_2$(μ-Ph_2PPy)$_2$](BF_4)$_2$ [15] and [Pd(η^3-2-CH_3-C_3H_4)(Ph_2PPy)$_2$](BF_4) [15] were prepared according to literature methods.

4.1. Ph_2PPy

^{1}H NMR (CD_2Cl_2, 298 K): δ 7.15 (m, 1H, H-3Py), 7.22 (m, 1H, H-5Py), 7.3–7.4 (m, 10H, phenyl), 7.60 (H-4Py), 8.71 (d, 1H, H-6Py, $J_{H\text{-}5Py\text{–}H\text{-}6Py}$ = 5.0 Hz). ^{31}P {^{1}H} NMR (CD_2Cl_2, 298 K): δ −3.5 (s). ^{13}C {^{1}H} NMR (CD_2Cl_2, 298 K): δ 164.0 (d, C-2Py, J_{PC} = 3.8 Hz), 150.5 (d, C-6Py, J_{PC} = 11.8 Hz), 136.8 (d, C-1Ph, J_{PC} = 10.7 Hz), 135.9 (d, C-4Py, J_{PC} = 3.0 Hz), 134.5 (d, C-2Ph, J_{PC} = 20.0 Hz), 129.3 (s, C-4Ph), 128.8 (d, C-3Ph, J_{PC} = 7.1 Hz), 128.2 (d, C-3Py, J_{PC} = 18.6 Hz), 122.5 (s, C-5Py).

4.2. [Ph_2PPyH](CH_3SO_3)

To a solution of 2-pyridyldiphenylphosphine in dichloromethane (150 mg, 0.57 mmol in 20 mL) were added 37 μL (55 mg, 0.57 mmol) of CH_3SO_3H under stirring. Addition of diethylether affords the pyridinium salt as a white microcrystalline powder (194 mg, 95% yield). Anal. Calc. for $C_{18}H_{18}NO_3PS$: C, 60.16; H, 5.05. Found: C, 60.2; H, 5.1%.

^{1}H NMR (CD_2Cl_2, 298 K): δ 2.50 (s, 3H, CH_3SO_3), 7.3–7.6 (m, 11H, phenyl and H-3Py), 7.82 (m, 1H, H-5Py), 8.22 (m, 1H, H-4Py), 9.18 (d, 1H, H-6Py, $J_{H\text{-}5Py\text{–}H\text{-}6Py}$ = 5.9 Hz), 14.0 (very br s, 1H, NH). ^{1}H NMR (CD_2Cl_2, 195 K): δ 2.34 (s, 3H, CH_3SO_3), 7.27 (m, 1H, H-3Py), 7.3–7.6 (m, 10H, phenyl), 7.82 (m, 1H, H-5Py), 8.22 (m, 1H, H-4Py), 9.11 (apparent t, 1H, H-6Py, $J_{H\text{-}5Py\text{–}H\text{-}6Py} \approx J_{NH\text{–}H\text{-}6Py} \approx$ 5 Hz), 17.05 (br d, 1H, NH, $J_{NH\text{–}H\text{-}6Py} \approx$ 5 Hz). ^{31}P {^{1}H} NMR (CD_2Cl_2, 298 K): δ −6.5 (s). ^{13}C {^{1}H} NMR (CD_2Cl_2, 298 K): δ 160.1 (d, C-2Py, J_{PC} = 31.6 Hz), 145.0 (d, C-6Py, J_{PC} = 3.6 Hz), 144.5 (s, C-4Py), 134.7 (d, C-2Ph, J_{PC} = 21.4 Hz), 131.4 (d, C-1Ph, J_{PC} = 8.8 Hz), 131.0 (s, C-4Ph), 130.9 (d, C-3Py, J_{PC} = 3.0 Hz), 129.7 (d, C-3Ph, J_{PC}= 8.2 Hz), 125.9 (s, C-5Py), 39.3 (s, CH_3SO_3).

4.3. [Pd(η^3-2-CH_3-C_3H_4)Cl(Ph_2PPyH)](CH_3SO_3) (***1a***)

2.0 μL of CH_3SO_3H (2.9 mg, 0.03 mmol) were added to a CD_2Cl_2 solution of **1** (13.7 mg, 0.03 mmol) in CD_2Cl_2 (1 mL).

^{1}H NMR (CD_2Cl_2, 253 K): δ 2.03 (s, 3H, CH_3), 2.51 (s, 3H, CH_3SO_3), 3.08 (s, H_b *anti*), 3.43 (br s, H_a *syn*), 3.70 (d, H_d *anti*, J_{HP} = 10.2 Hz), 4.63 (m, H_c *syn*, J_{HP} = 6.5 Hz), 7.5–7.7 (m, 11H, phenyl and H-3Py), 7.96 (m, 1H, H-5Py), 8.32 (m, 1H, H-4Py), 9.24 (m, H-6Py, $J_{H\text{-}5Py\text{–}H\text{-}6Py}$ = 3.3 Hz), 11.9 (br s, 1H, NH). ^{31} P{^{1}H} NMR (CD_2Cl_2, 253 K): δ 26.8 (s). ^{13}C NMR ($CDCl_3$, 298 K): δ 153.4 (d, C-2Py, J_{CP} = 33.5 Hz), 146.0 (d, C-6Py, J_{CP} = 6.5 Hz), 143.4 (d, C-4Py, J_{CP} = 4.2 Hz), 134.6 (br d, C-2all, J_{CP} = 3.0 Hz), 134.2 (d, C-2Ph, J_{CP} = 14.3 Hz), 131.9 (d, C-4Ph, J_{CP} = 1.6 Hz), 131.4 (d, C-3Py, J_{CP} = 10.4 Hz), 129.4 (d, C-3Ph, J_{CP} = 10.4 Hz), 128.0 (d, C-1Ph, J_{CP} = 41.7 Hz), 127.0 (s, C-5Py), 79.6 (br s, C-3all), 62.3 (br s, C-1all), 39.1 (s, CH_3SO_3), 23.2 (s, C-4all).

4.4. [Pd(η^3-2-CH_3-C_3H_4)(PPh_2PyH)$_2$](BF_4)(CH_3SO_3)$_2$ (***3a***)

4.0 μL of CH_3SO_3H (5.8 mg, 0.06 mmol) were added to a CD_2Cl_2 solution of **3** (23.3 mg, 0.03 mmol) in CD_2Cl_2 (1 mL).

^{1}H NMR (CD_2Cl_2, 298 K): δ 1.97 (s, 3H, CH_3), 2.73 (6H, CH_3SO_3), 3.90 (m, 2H, H_b and H_d *anti*), 3.93 (br s, 2H, H_a and H_c *syn*), 7.3–7.7 (m, 26H, arom), 8.17 (t, 2H, H-4Py, $J_{H\text{-}4Py\text{–}H\text{-}5Py} \approx J_{H\text{-}4Py\text{–}H\text{-}3Py}$ = 7.7 Hz), 8.32 (d, 2H, H-6Py, $J_{H\text{-}5Py\text{–}H\text{-}6Py}$ = 4.4 Hz), 13.2 (br s, 2H, N-H). ^{31}P{^{1}H} NMR (CD_2Cl_2, 298 K): δ 26.6 (s). ^{13}C{^{1}H} NMR (CD_2Cl_2, 298 K): δ 152.3 (AA′X′ m, 2C, C-2Py), 147.4 (AA′X m, 2C, C-6Py), 142.6 (s, 2C, C-4Py), 140.0 (t, 1C, C-2all, J_{CP} = 5.0 Hz), 134.4 (AA′X m, 8C, C-2Ph), 132.7 (s, 4C, C-4Ph), 129.9–129.7 (m, 10C, C-3Ph and C-3Py), 127.6 (AA′X m, 2C, C-1Ph), 127.1 (s, 2C, C-5Py), 80.6 (AA′X m, 2C, C-1all and C-3all), 39.5 (s, 2C, CH_3SO_3), 23.2 (s, 1C, C-4all).

4.5. [Pd(η^2-fumaronitrile)(PPh_2Py)$_2$] (***4***)

To a solution of **3** (332 mg, 0.43 mmol) in dichloromethane (20 mL) were added first 39 mg (0.50 mmol) of fumaronitrile then 135 μL (95 mg, 1.25 mmol) of diethylamine dissolved in 10 mL of dichloromethane. After stirring for 1 h the solution was extracted with water (2 × 20 mL), dried over $MgSO_4$ and filtered. The clear

dichloromethane solution was concentrated to small volume under reduced pressure. Addition of *n*-hexane afforded **4** as a yellow solid (230 mg, 75% yield). Anal. Calc. for $C_{38}H_{30}N_4P_2Pd$: C, 64.19; H, 4.25. Found: C, 64.1; H, 4.3%.

^{1}H NMR (CD_2Cl_2, 298 K): δ 3.19 (AA′XX′ m, 2H, =CH), 7.13–7.19 (m, 4H, H-1Py and H-2Py), 7.20–7.55 (m, 20H, arom), 8.54 (d, 2H, H-6Py, $J_{H\text{-}5Py\text{–}H\text{-}6Py}$ = 4.4 Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K): δ 27.6 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K): δ 159.7 (d, 2C, C-2Py, J_{PC} = 57.6 Hz), 150.4 (AXX′ m, 2C, C-6Py), 135.8 (AXX′ m, 2C, C-4Py), 134.7 (AXX′ m, 4C, C-2Ph), 134.0 (AXX′ m, 4C, C-2Ph), 133.9 (AXX′ m, 2C, C-1Ph), 133.0 (AXX′ m, 2C, C-1Ph), 130.3 (s, 2C, C-4Ph), 130.2 (s, 2C, C-4Ph), 128.8–128.3 (m, 10C, C-3Ph and C-3Py), 123.5 (s, 2C, C-5Py), 121.3 (br s, 2C, CN), 33.7 (br AXX′ m, 2C, C=C).

4.6. [Pd(η^2-fumaronitrile)($PPh_2PyH)_2$]($CH_3SO_3)_2$ (**4a**)

A cold (−70 °C) solution of complex **4** (18 mg, 0.025 mmol) in CD_2Cl_2 (1 mL) was treated with 3.3 μl of CH_3SO_3H (4.9 mg, 0.05 mmol).

^{1}H NMR (CD_2Cl_2, 253 K): δ 2.53 (s, 6H, CH_3SO_3), 3.53 (AA′XX′ m, =CH), 7.16–7.62 (m, 22H, phenyl and H-3Py), 7.67 (m, 2H, H-5Py), 8.11 (m, 2H, H-4Py), 8.61 (br s, 2H, H-6Py), 10.7 (br s, 2H, NH). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 253 K): δ 26.4 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 233 K): δ 151.9 (d, 2C, C-2Py), 145.5 (AXX′ m, 2C, C-6Py), 145.3 (AXX′ m, 2C, C-4Py), 135.1 (d, 4C, C-2Ph, J_{PC} = 17.0 Hz), 132.7 (d, 4C, C-2Ph, J_{PC} = 15.5 Hz), 132.3 (s, 2C, C-4Ph), 131.7 (s, 2C, C-4Ph), 129.9 (s, 2C, C-3Py), 129.60 (d, 4C, C-3Ph, J_{PC} = 4.6 Hz), 129.46 (d, 4C, C-3Ph, J_{PC} = 4.9 Hz), 128.0 (d, 2C, C-1Ph, J_{PC} = 37.6 Hz), 127.4 (s, 2C, C-5Py), 126.2 (d, 2C, C-1Ph, J_{PC} = 37.6 Hz), 119.34 (s, 1C, CN), 119.29 (s, 1C, CN), 38.8 (s, 2C, CH_3SO_3), 36.5 (br AXX′ m, 2C, C=C).

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