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Acid–base behaviour of organopalladium complexes [Pd(CNN)R]BF_4

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Protonation of the orthopalladated carbon of the cyclometallated complex $[Pd(CNN)L]^+$, where L = $P(OMe)_3$ and HCNN is the C-deprotonated form of the tricoordinated chelant donor ligand 2-acetylpyridinephenylhydrazone, has been studied at 25, 35, 40 and 45 °C in highly acidic 10% v : v ethanol–water, and at 25 °C in 30% and 50% v : v ethanol–water. The acidity constants pK_{SH}^{2+} remained essentially constant with temperature, whereas these values noticeably increased with decreasing water content. Likewise, the complexes with L = $P(OPh)_3$, PPh_3, and SC_4H_8 were also studied at 25 °C in 10% v : v ethanol–water. Under such conditions the pK_{SH}^{2+} values were more negative in the order SC_4H_8 < PPh_3 < $P(OMe)_3$ < $P(OPh)_3$; in the case of phosphines, this feature can be attributed to the substituent π-acceptor ability. These complexes behave as very weak bases and the reactions occur in sulfuric acid stronger than 1.3 M; the medium effects observed in the spectral curves were corrected to reliably determine the pK_{SH}^{2+} values. The observed difference in the solvation parameter m^* can be related to the differing hardness of the ligands bound to Pd.

Introduction

Cyclometallated complexes constitute an important tool to activate the C–H σ bond to form transition-metal complexes; these structures have been suggested as intermediate species in metal-catalyzed chemical reactions.[1] In particular, the highly reactive carbon-metal σ bond of cyclopalladated complexes becomes stabilized by further coordination of a donor heteroatom to the metal centre. This class of compounds manifests quite a rich chemistry;[2–6] some stable cyclometallated complexes are regarded as "frozen" intermediates, and their structures may provide a valuable source of mechanistic information.[7] A wide range of reactions involving cyclometallated compounds proceed with noticeable regio- and stereoselectivity.[8–11] Most compounds possess colour centres susceptible to proton transfer, and may undergo acidic and basic hydrolysis.[12]

Despite the interest of the chemistry of cyclopalladated compounds, so far only very few kinetic and thermodynamic contributions have appeared, of which none was performed in highly acidic media.[13] Knowledge of the dissociation constants is essential to reliably establish the hydrolysis mechanisms. In this work the stability and acid–base behaviour of a set of four cyclopalladated complexes (shown in Fig. 1): $[Pd(CNN)L]BF_4$, where L = $P(OMe)_3$, $P(OPh)_3$, PPh_3 and SC_4H_8, 2-acetylpyridinephenylhydrazone (HCNN) being a tricoordinated chelant donor ligand (D), were studied in concentrated sulfuric acid. In basic medium the ligand remains stable. In highly acidic media the kinetics of the acid hydrolysis of the ligand (D) was investigated using a set of mixed solvents, the reaction rate decreasing with increasing solvent permittivity.[14] The protonation of the $[Pd(CNN)P(OMe)_3]BF_4$ complex was studied over the 25–45 °C temperature range in highly acidic 10%, 30%, and 50% v : v ethanol–water; the other complexes were studied at 25 °C in 10% ethanol–water.

Results

Evaluation of the relative basicities and protonation parameters of weak organic bases has attracted a deal of interest both as a source of information on the molecular electronic structure and as a tool to interpret the reactivity of acid-catalyzed chemical reactions. The protonation equilibria in highly acidic media for the Pd complexes investigated can be represented by eqn. (1):

$$SH^{2+} \overset{K_{SH^{2+}}}{\rightleftharpoons} S^+ + H^+ \qquad (1)$$

where SH^{2+} represents the protonated complex and S^+ the cationic, unprotonated form of the four complexes (substrate). The equilibrium constant can then be described in terms of the ionization constant pK_{SH}^{2+} of the protonated form, using eqn. (2):

$$pK_{SH}^{2+} = \log I - \log C_H{}^+ - \log (\gamma_H{}^+ \gamma_S{}^+ / \gamma_{SH}{}^{2+}) \qquad (2)$$

where $C_H{}^+$ stands for the hydrogen ion concentration, and $I = [SH^{2+}]/[S^+]$ represents the ionization ratio. Ionization ratios can be experimentally evaluated by measuring the variation with medium acidity of a particular property of the SH^{2+} species compared to that of the unprotonated form, S^+; among the properties most commonly used are UV-visible, ^1H and ^{13}C NMR measurements.[15]

The protonation constant pK_{SH}^{2+} was determined by collecting and putting together the first spectral curve recorded at time $t = 0$ of each kinetic run of a set of hydrolysis experiments, each performed at a different solution acidity. The changes observed in the first spectral curves, brought about by stepwise increase of medium acidity, enables establishment of the (temperature-independent) acidity ranges, 4.54–11.67 M sulfuric acid in 10% v : v EtOH–H_2O, 5.04–10.09 M in 30% v : v EtOH–H_2O, and 6.12–9.01 M in 50% v : v EtOH–H_2O for protonation of the $[Pd(CNN)P(OMe)_3]^+$ complex; as an example, the set of first spectral curves corresponding to dissociation of its protonated form in 30% v : v EtOH–H_2O are collected in Fig. 2(a), the pattern with the other solvents being similar. Regarding the other three complexes, $[Pd(CNN)P(OPh)_3]^+$ protonates in 5.18–11.67 M sulfuric acid,

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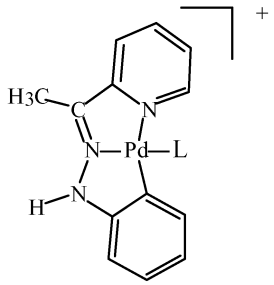


L: $P(OMe)_3$, $P(OPh)_3$, PPh_3, SC_4H_8

Fig. 1 The $[Pd(CNN)R]BF_4$ complexes.

$[Pd(CNN)PPh_3]^+$ in 3.89–11.02 M sulfuric acid, and $[Pd(CNN)SC_4H_8]^+$ in 1.30–11.02 M sulfuric acid in 10% EtOH–H_2O. Appearance of distorted isosbestic points [Fig. 2(a)] reveals the presence of at least two species in equilibrium; in fact the UV spectral curves recorded exhibited shifts in wavelengths that could in principle be ascribed either to hydrolysis, or to medium effects, or both.

This notwithstanding, hydrolysis effects can be discarded since the spectral curves were recorded by a very fast technique compared to the timescale of the hydrolysis reaction. The medium effects were suitably analyzed by the Cox–Yates and vector analysis methods.

(I) Analysis of medium effects. The Cox–Yates method.

This method, developed by Cox *et al.*[16] from an earlier approach,[17,18] involves introduction of the excess acidity function X (or medium parameter); X represents the difference between the observed acidity and that of the system if it behaves ideally,[19] and is based on the free energy relationship:

$$\log I - \log C_{H^+} = m^*X + pK_{SH^{2+}} \qquad (3)$$

the X acidity scales being constructed for strongly acidic solutions (with water as a reference solvent) using a set of differently structured bases whose protonation acidity ranges overlap stepwise. The parameter m^*, or solvation coefficient, accounts for the susceptibility of the protonated base to be stabilized by solvation, especially by H-bonding, and reflects the behaviour of the set of bases. Experimental and theoretical aspects of this issue have been extensively treated.[14–28] Evaluation of the X function in 10% ethanol–water at temperatures different from 25 °C, required use of the X function in water[22,23] and the relationship $X_T = X_{298.15}\,(298.15/T)$,[24] but the results provided (not shown) agreed only poorly with those from other acidity functions. Under I in Table 1 are listed the $pK_{SH^{2+}}$ values provided in 10% ethanol–water at 25 °C; due to the limited capability of the program used, the results may vary with the particular range of wavelengths, hence the constant value was averaged.

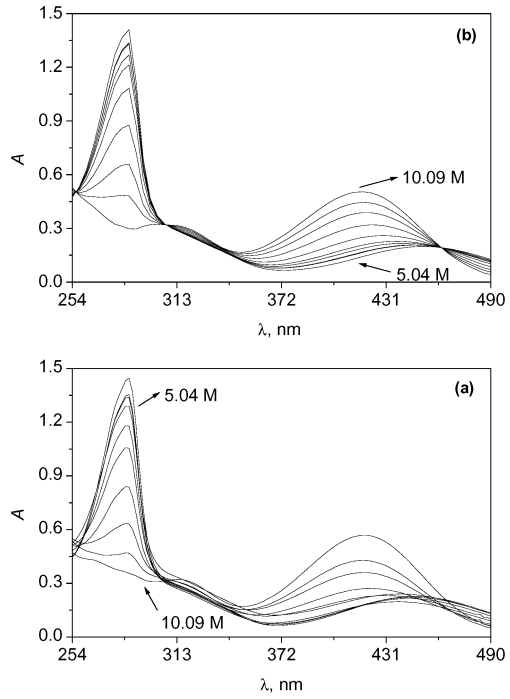


Fig. 2 (a) Spectral curves corresponding to protonation of $[Pd(CNN)P(OCH_3)_3]^+$ at 25 °C in 30% v:v ethanol–water. (b) Reconstituted absorbances after application of vector analysis.

(II) Correction of medium effects by vector analysis

Vector analysis has been used successfully to correct the medium effects observed in the protonation of amides,[25,26] hydroxamic acids,[27] pyrimidines[28] and hydrazones;[14] decomposition of the absorbance readings into the minimum number of independent components capable of reproducing the spectral curves, allows reliable ionization ratios to be obtained. The absorbance A, measured at n different acidity levels and r wavelengths, were arranged into an $(n \times r)$ matrix array; if p independent components are needed to reproduce the experimental curves, then the absorbance readings at each wavelength and C_{H^+} acidity level can be expressed by the set of eqns. (4):

$$\begin{aligned} A_1 &= \overline{A_1} + c_1v_{11} + c_2v_{21} + \ldots\ldots + c_pv_{p1} \\ A_2 &= \overline{A_2} + c_1v_{12} + c_2v_{22} + \ldots\ldots + c_pv_{p2} \\ &\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \\ A_r &= \overline{A_r} + c_1v_{1r} + c_2v_{2r} + \ldots\ldots + c_pv_{pr} \end{aligned} \qquad (4)$$

where $\bar{A}_r$ is the averaged absorbance measured at a particular wavelength and C_{H^+} value, $\boldsymbol{v}_{pr}$ are the characteristic vectors, and c_p the weighing factors (or fitting coefficients). In practice only two characteristic vectors are sufficient to describe the total effect, the first vector ($\boldsymbol{v}_{1r}$) accounting for the change of acidity, and the second ($\boldsymbol{v}_{2r}$) for the medium effect upon protonation.[25] Table 2 lists the c_1 coefficients determined over the wavelength range used; to attain consistent results the calculations were repeated introducing readings over other different ranges.

If c_{1,S^+} and $c_{1,SH^{2+}}$ are the coefficients for the fully unprotonated and fully protonated base, then the ionization ratios can be evaluated readily with eqn. (5):

$$I = (c_{1,SH^{2+}} - c_1)/(c_1 - c_{1,S^+}) \qquad (5)$$

where c_1 are the coefficients at intermediate extents of protonation; Figs. 2(b) to 5 show the absorbance curves reconstituted by vector analysis. Once the c_1 characteristic vectors had been evaluated as a function of C_{H^+}, to determine accurate $pK_{SH^{2+}}$ values, the thermodynamic equations described in the following two sections were used.

(IIa) Excess acidity analysis. In strongly acidic solutions two parameters are needed to fully describe the strength of a base: $pK_{SH^{2+}}$ and m^*. The need for these parameters stems from the stabilization of SH^{2+} by internal delocalization of the cationic charge and by external solvation effects. By a process similar to that of Chandler and Lee,[29] introduction into eqns. (3) and (5) of the c_1 coefficients results in eqn. (6):

$$c_1 = \frac{c_{1,S^+} - c_{1,SH^{2+}}}{1 - C_{H^+}10^{m^*X + pK_{SH^{2+}}}} + c_{1,SH^{2+}} \qquad (6)$$

This procedure requires introducing initial c_{1,S^+}, $c_{1,SH^{2+}}$, m^*, and $pK_{SH^{2+}}$ values, the latter being evaluated with the X functions available at 25 °C for aqueous sulfuric acid;[30] Table 3

Table 1 Protonation parameters determined with (I) the Cox–Yates method for correction of medium effects and (II) vector analysis using different thermodynamic equations. Method (III): mean pK_{SH}^{2+} values determined from the individual values of methods I and II

Method	T/°C	Acidity function	$[Pd(CNN)P(OMe)_3]^+$		$[Pd(CNN)P(OPh)_3]^+$		$[Pd(CNN)PPh_3]^+$		$[Pd(CNN)SC_4H_8]^+$	
			pK_{SH}^{2+}	m or m^*	pK_{SH}^{2+}	m or m^*	pK_{SH}^{2+}	m or m^*	pK_{SH}^{2+}	m or m^*
10% EtOH–H_2O										
I	25	X[30]	−4.6 ± 0.3	1.21 ± 0.09	−5.0 ± 0.4	0.82 ± 0.01	−2.6 ± 0.2	0.86 ± 0.01	−2.2 ± 0.1	0.9 ± 0.2
IIa Cox–Yates [eqn. (6)]	25	X[30]	−4.2 ± 0.2	1.1 ± 0.1	−4.5 ± 0.4	0.72 ± 0.08	−2.4 ± 0.2	0.67 ± 0.06	−2.0 ± 0.4	1.1 ± 0.3
IIb Hammett–Deyrup	25	H_0[33]	−4.2 ± 0.3	1.0 ± 0.1	−4.8 ± 0.5	0.81 ± 0.09	−2.9 ± 0.1	0.76 ± 0.06	−2.0 ± 0.5	1.1 ± 0.2
[eqn. (9)]	25	H_0[34]	−4.3 ± 0.3	0.9 ± 0.1	−4.8 ± 0.5	0.81 ± 0.09	−2.6 ± 0.2	0.76 ± 0.05	−2.0 ± 0.5	1.1 ± 0.3
	35	H_0[33]	−4.3 ± 0.3	1.1 ± 0.2						
	40	H_0[35]	−4.1 ± 0.1	1.1 ± 0.1						
	45	H_0[33]	−4.1 ± 0.2	1.1 ± 0.1						
30% EtOH–H_2O										
IIc Hammett–Deyrup	25	H_0[36]	−5.3 ± 0.1	0.7 ± 0.1						
[eqn. (9)]	25	H_{dip}[37]	−5.0 ± 0.2	0.8 ± 0.1						
50% EtOH–H_2O										
IId Hammett–Deyrup [eqn. (9)]	25	H_0[40]	−6.5 ± 0.3	0.7 ± 0.2						

		pK_{SH}^{2+} at % EtOH–H_2O					
		$[Pd(CNN)P(OMe)_3]^+$			$[Pd(CNN)P(OPh)_3]^+$	$[Pd(CNN)PPh_3]^+$	$[Pd(CNN)SC_4H_8]^+$
Method	T/°C	10%	30%	50%	10%	10%	10%
III	25	−4.2 ± 0.2	−5.2 ± 0.1	−6.5 ± 0.3	−4.9 ± 0.4	−2.8 ± 0.1	−2.0 ± 0.4
	30	−4.3 ± 0.4					
	35	−4.3 ± 0.4					
	40	−4.1 ± 0.5					
	45	−4.1 ± 0.5					

lists the polynomial coefficients of the X *vs.* C_{H^+} fitting. A few iterations were sufficient to attain convergence, the minimum chi-square value being a criterion for the goodness of the fits. Part IIa in Table 1 summarizes the results; $m^* = 0$ represents the upper limit of the solvation requirements on this scale (in water, H_3O^+ has the highest solvation requirements, and $m^* = 0$), whereas higher m^* values denote weaker solvation.[18] The value $m^* = 0.90$ (25 °C) deduced as an average of the values listed in part IIa of Table 1 is noticeably higher than the $m^* = 0.56$ for protonation of hydroxamic acids in $HClO_4$, 0.63 in H_2SO_4,[27] and 0.51 for protonation of amides,[26] and is close to $m^* = 1.0$ for primary aromatic amines and $m^* = 0.8$ for carbocations.[22] The m^* value of the complexes, compared to that of the HCNN ligand (D; $m^* = 0.94$[14]), reveals similar solvation requirements. Regarding acidity constants, the ligand undergoes protonation at the pyridine N site ($pK_{DH}^+ = 4.9$) and, at somewhat higher acidity, at the imine N site ($pK_{DH2}^{2+} = -5.8$, 25 °C, 10% ethanol–water).[14] With this in mind, the average value (given in III in Table 1) denotes that the complex basicity strongly depends on the substituent and, as a rule, the complex becomes a stronger base compared to the ligand.

(IIb) The Hammett equation. Although eqn. (2) is thermodynamically exact, evaluation of the unknown molar activity coefficient ratio terms, γ_i constitutes a major difficulty. The first researchers to tackle this problem were Hammett and Deyrup,[31a] and further revised by other researchers[31b–d] who defined the H_0 acidity function in the form:

$$mH_0 = -\log I + pK_{SH}^{2+} \quad (7)$$

Table 2 Coefficients c_1 determined by vector analysis [eqn. (8)] at different temperatures and in 10%, 30% and 50% ethanol–water mixed solvents

$[Pd(CNN)P(OMe)_3]^+$									$[Pd(CNN)P(OPh)_3]^+$		$[Pd(CNN)PPh_3]^+$		$[Pd(CNN)SC_4H_8]^+$	
10%					30%		50%		10%		10%		10%	
M	25 °C	35 °C	40 °C	45 °C	M	25 °C	M	25 °C	M	25 °C	M	25 °C	M	25 °C
3.89		−0.326			5.04	0.349	6.12	−0.380	7.78	0.276	1.945	−0.329	1.297	0.49
4.54	0.298	−0.312	−0.389	−0.373	6.05	0.287	6.48	−0.407	8.43	0.272	3.890	−0.349	2.593	0.432
5.19	0.300				6.56	0.282	6.84	−0.200	9.73	0.204	5.187	−0.269	3.242	0.38
5.84	0.306	−0.293	−0.346	−0.365	7.06	0.229	7.20	−0.209	10.05	0.19	5.835	−0.252	3.890	0.077
6.48	0.304	−0.263	−0.345	−0.338	7.56	0.183	7.56	−0.115	10.70	0.12	6.484	−0.191	4.538	−0.025
7.13	0.246				8.07	0.072	7.92	0.084	11.02	0.077	7.132	−0.101	5.187	−0.093
7.78	0.189	−0.211	−0.219	−0.241	8.57	−0.101	8.29	0.176	11.67	−0.027	7.780	0.004	5.835	−0.237
8.10	0.114				9.08	−0.285	8.65	0.457	13.29	−0.346	9.077	0.222	7.780	−0.285
8.43	0.041	−0.035	−0.091	−0.067	9.58	−0.434	9.01	0.588	14.26	−0.36	9.725	0.339	8.104	−0.367
9.08	−0.075	0.158	0.136	0.119	10.09	−0.588			14.91	−0.436	10.698	0.465	8.429	−0.377
9.73	−0.204	0.289	0.329	0.349					15.56	−0.448	11.022	0.455		
10.05	−0.227													
10.37	−0.287	0.489	0.411	0.445										
10.70	−0.343													
11.02	−0.336	0.503	0.508	0.466										
11.67	−0.335													

Table 3 Fitting coefficients, a_i, of the polynomial functions: M, sulfuric acid concentration; w, H_2SO_4 to H_2O weight percentage; c_{H^+}, proton concentration; r, correlation coefficient

	$\%w^{48}$	$\log c_{H^+}{}^{30}$	X^{30} (25 °C)	$H_0{}^{33}$ (25 °C)	$H_0{}^{34}$ (25 °C)	$H_0{}^{33}$ (35 °C)	$H_0{}^{35}$ (40 °C)	$H_0{}^{33}$ (45 °C)	$H_0{}^{36}$ (25 °C)	$H_0{}^{37}$ (25 °C)	$H_0{}^{40}$ (30 °C)
a_0		0.079997579	0.02785299	$6.01594 \cdot 10^{-1}$	0.19474	0.56181	0.67046	0.55537	0.0267553	−1.3563382	0.466
a_1	9.787	0.47124845	−0.23469055	$-1.09376 \cdot 10^{-1}$	−0.47989	−0.10215	−0.12556	−0.10124	−0.3561399	0.8530588	−0.831
a_2	-5.781×10^{-1}	−0.11436307	0.22870050	$2.19357 \cdot 10^{-3}$	−0.00014	0.00183	0.00278	0.00180	1.2318681		
a_3	3.749×10^{-2}	0.24168572	0.03258271	$-3.99851 \cdot 10^{-5}$	−0.00021	$-3.308 \cdot 10^{-5}$	$-4.609 \cdot 10^{-5}$	$3.231 \cdot 10^{-5}$			
a_4	-1.710×10^{-3}	−0.24539207	−0.04026123	$1.81528 \cdot 10^{-7}$		$1.409 \cdot 10^{-7}$	$1.978 \cdot 10^{-7}$	$1.374 \cdot 10^{-7}$			
a_5	3.145×10^{-5}	0.13149242	−0.00087414								
a_6	2.654×10^{-7}	−0.03643644	0.00555282								
a_7		0.00401342									
r		0.9999	0.9999	0.9998	0.9997	0.9993	0.9998	0.9999	0.9999	0.9953	0.9999

Functions

$\%w^{48} = a_1M + a_2M^2 + a_3M^3 + a_4M^4 + a_5M^5 + a_6M^6$

$\log c_{H^+}{}^{30} = a_0 + a_1(\ln M) + a_2(\ln M)^2 + a_3(\ln M)^3 + a_4(\ln M)^4 + a_5(\ln M)^5 + a_6(\ln M)^6 + a_7(\ln M)^7$

$X^{30} = (a_0 + a_2M + a_4M^2 + a_6M^3)/(1 + a_1M + a_3M^2 + a_5M^3)$

$H_0{}^{33,35} = a_0 + a_1w + a_2w^2 + a_3w^3 + a_4w^4$

$H_0{}^{34} = a_0 + a_1M + a_2M^2 + a_3M^3$

$H_0{}^{36} = a_0 + a_1M^{a_2}$

$H_0{}^{37} = a_0 + a_1M$

$H_0{}^{40} = a_0 + a_1M;\ M > 2$

The acidity function H_0 defined with aniline derivatives as a reference base (B):

$$H_0 = -\log a_{H^+}\, \gamma_B/\gamma_{BH^+} \quad (8)$$

depends on the temperature range, the mineral acid, and the solvent used. If for a set of overlapping bases the relationship $\gamma_B/\gamma_{BH^+} = \gamma_{S^+}/\gamma_{SH^{2+}}$ is fulfilled at a particular acidity level, then the Hammett cancellation assumption applies, yielding $m = 1$ in eqn. (7); therefore, the closer m tends to unity, the more accurately the $pK_{SH^{2+}}$ value can be deduced. By a process similar to eqn. (6), from eqns. (5) and (7) it follows that:

$$c_1 = \frac{c_{1,S^+} - c_{1,SH^{2+}}}{1 - 10^{-mH_0 + pK_{SH^{2+}}}} + c_{1,SH^{2+}} \quad (9)$$

In this work a set of acidity functions for sulfuric acid in ethanol–water mixtures is required. Considering that the effect of ethanol on pH measurements is negligible in 10% ethanol–water,[32] the effect on the acidity function should also be negligible; hence, in 10% ethanol–water the H_0 values used were those defined in aqueous solution.[33–35]

Application of eqn. (9) requires a fair H_0 *vs* C_{H^+} correlation corresponding to c_1. Table 3 lists the fitting coefficients of the acidity functions with C_{H^+}; H_0 was evaluated at the same set of different acid molarities related to c_1. The c_1 *vs.* $-H_0$ plot at 25 °C (Fig. 6) and its fitted curve show the typical S-shaped curve of a complete equilibrium. Part IIb in Table 1 lists the p$K_{SH^{2+}}$ and m* values determined with eqn. (9) for the $[Pd(CNN)P(OMe)_3]^+$ complex in 10% ethanol–water at 25, 35, 40 and 45 °C and in 10% ethanol–water at 25 °C for the other complexes.

The acidity functions H_0 and H_{dip},[36] (defined with diphenylamine as a reference base) were proved to efficiently describe the complex behaviour at 25 °C in 30% ethanol–water over an acidity range close to that used in this work;[37] in accordance with the Hammett assumption they yielded m values close to unity (part IIc in Table 1). H_{azo},[38] based on azobenzenes, and H_A,[39] based on amides, were also tested, but they yielded values for m* far from unity [eqn. (9)], hence these functions do not describe properly the acid–base behaviour of the complex. For 50% ethanol–water, only a single function at 25 °C was found that could cover the full protonation 4.5–11.7 M H_2SO_4 acidity range (part IId in Table 1).[40] Acidity functions at other temperatures and 30% and 50% ethanol–water were not available. Fig. 7 plots H_0 *vs.* H_2SO_4 concentration at 25 °C in different solvents; only for low ethanol content were the H_0 values solvent independent, revealing that the free energy relationship for aqueous solutions can be extended to mixed solvents only at low acid concentration.

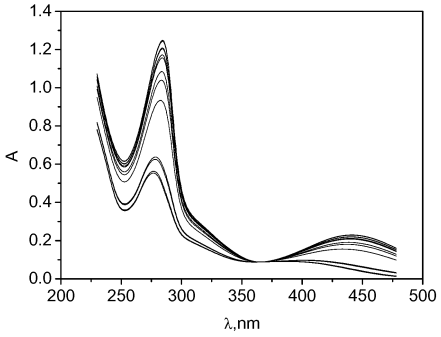


Fig. 3 Reconstituted absorbances after application of vector analysis to $[Pd(CNN)P(OPh)_3]^+$

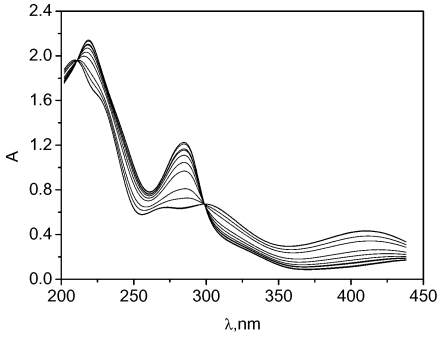


Fig. 4 Reconstituted absorbances after application of vector analysis to $[Pd(CNN)PPh_3]^+$

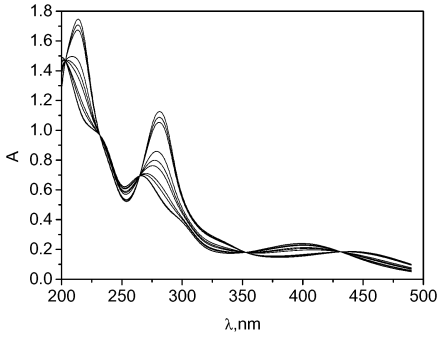


Fig. 5 Reconstituted absorbances after application of vector analysis to $[Pd(CNN)SC_4H_8]^+$

Discussion

The results provided by the Hammett and excess acidity methods are in good agreement. This provides support for the idea that the acidity functions X [eqn. (3)] and H_0 [eqn. (8)] describe properly the Pd organometallic complexes investigated; although these complexes differ structurally from the organic bases used to define the acidity functions, this finding demonstrates the wide applicability of both the acidity functions and the methods employed.

As shown above, the complexes investigated displayed only a single acid–base equilibrium. Substitution of ligand L by H^+ can be discarded since the 14-electron complex that would be produced should be quite unstable, otherwise the substituent should be released as a cation species, which is unlikely. The CNN ligand contains four sites (three N and one orthopalladated C) susceptible to protonation in strongly acidic medium. Pd(II) is electrophilic in nature and the pyridine and imine N sites are nucleophilic, hence they may form σ bonds by transfer of lone electron pairs to the empty metal orbitals; as a consequence the basicity of both N sites (pyridine and imine) are lowered and become susceptible to nucleophilic attack, hence protonation is unlikely. In summary, only the non-coordinated N (NH) and the orthopalladated C are feasible as protonation sites, and the two processes are compatible with complex hydrolysis. If the N (NH) site becomes protonated, then an –I effect on the adjacent imine N would appear, with the result of a lowering of its basicity and, as a consequence, a lowering of the stability of the C–Pd bond, with further decomposition of the complex. Actually, intramolecular coordination to the heteroatom stabilizes the organometal bond in cyclometallated compounds.[8] Likewise, C protonation would cause breaking of the C–Pd bond and subsequent decomposition of the complex; organometallic ligands can be polarized upon bonding to metal and become activated, weakened, or even broken by chemical reactions.[41a]

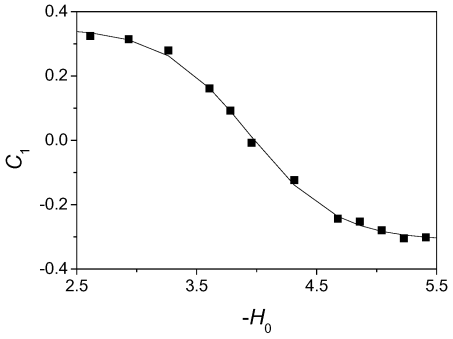


Fig. 6 c_1 *vs.* H_0[33] plot, eqn. (9), for $[Pd(CNN)P(OCH_3)_3]^+$; T = 25 °C, 10% v : v ethanol–water.

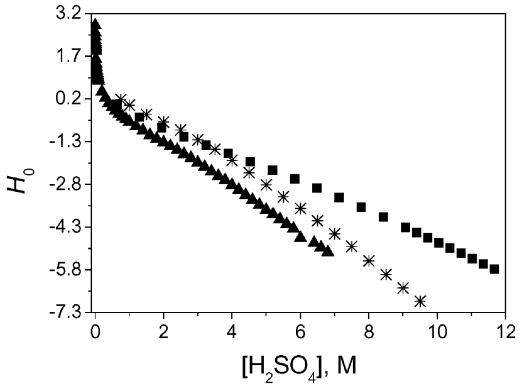


Fig. 7 Plot of H_0 *vs.* H_2SO_4 concentration in different solvents: (■) water,[33] (*) 30% v : v ethanol–water,[37] (▲) 50% v : v ethanol–water.[40]

Substituent effects

The preferred protonation site (uncoordinated N *vs.* orthopalladated C) can be determined by analyzing the substituent effect on the pK_{SH}^{2+} constant. The data in Table 1, part III, reveal that, at 25 °C and in 10% EtOH–water, the acidity of the complexes increase (more negative pK_{SH}^{2+} values) in the order: $SC_4H_8 < PPh_3 < P(OMe)_3 < P(OPh)_3$. Phosphines are π acids to an extent that depends on the nature of the R groups present on the PR_3 ligand (L). For alkyl phosphines, the π acidity is weak, and the aryl and alkoxy groups are successively more effective in promoting the π acidity. The σ* orbital of the P–R bonds are assumed to play the role of acceptor in PR_3.[42] The more electronegative the R substituent, the more stable becomes the orbital used by the R fragment to bind phosphorus, therefore the σ* orbital of the P–R bond also becomes more stable. Likewise, the P contribution to σ* increases, as does the size of the σ* lobe that points toward the metal; these effects make the empty σ* more accessible for back-donation. The final order of the π-acid character, $PPh_3 < P(OMe)_3 < P(OPh)_3$,[41b] coincides with the order of decrease of pK_{SH}^{2+} of phosphines (shown above), consistent with the observed increase of acidity, that is the decrease of basicity of the protonated atom. It can then be inferred that the electronic density of the protonated atom is in reverse order to the π-acceptor character of the substituent. This relationship can be established with the C directly linked to Pd and, to a lower extent, with the N non-coordinated to Pd. The complex involving SC_4H_8 is the strongest base, indicating that the electronic density on the corresponding C site is higher than in phosphines, consistent with the substituent electronegativity. Thus, the suggested reaction involves protonation of the orthopalladated C site, breaking of the organometal bond, and addition to the coordination sphere of a solvent molecule (EtOH or water).

Solvent effects

The pK_{SH}^{2+} values were evaluated for each temperature and solvent composition as the average value of those deduced with all functions used. For $[Pd(CNN)P(OMe)_3]^+$, an increase in water content causes pK_{SH}^{2+} to increase from −6.5 to −4.4 at 25 °C (see part III, Table 1). The solvation effect plays a crucial role since the reaction is ionic in nature, the reactant is a monocation, and the product a dication; this effect has been established through the m^* parameter [eqn. (3)]. It should be recalled that a large m^* value denotes a larger difference from H_3O (for which $m^* = 0$) and hence weaker solvation.[22] The m^* data of Table 2 indicate that solvation increases in the order $SC_4H_8 = P(OMe)_3 < P(OPh)_3 < PPh_3$.

The qualitative magnitude of m^* can be understood in terms of stabilization of the protonated base by H-bonding under the

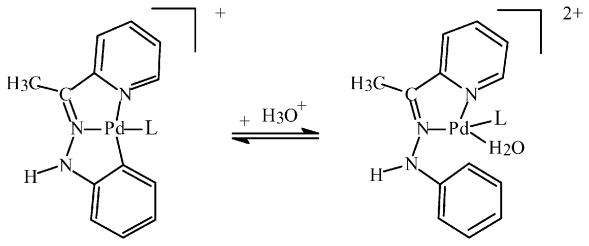
influence of several factors: (i) the degree of charge localization on an electronegative atom forming a solvation site; (ii) the nature of the atom; (iii) the number of hydrogens bound at the H-bonding site; and more rarely (iv) steric hindrance to solvation.[22] Phosphorus and sulfur atoms have a lone pair that can be donated to a metal, however, the electron and steric properties of the ligands can be modified depending on the particular atom bound; for tertiary phosphines (PR_3) they are predictable over a very wide range by varying R. For PR_3 and SC_4H_8 the connection is not immediate.

The dependence of the electronic effect of various PR_3 ligands on the nature of the R group has been quantified by Tolman,[43] who concluded that the donor character of phosphines increases in the order $P(OPh)_3 < P(OMe)_3 < PPh_3$, hence this order should be the same for the solvation decrease as a result of the partial compensation of the positive Pd charge; in fact the m^* values deduced do not follow the above sequence. As already stated, the steric factor can influence the m^* values and become even more relevant. Tolman[43] has also quantified the steric effects of phosphines with his *cone angle*; this is obtained by taking a space-filling model of the $M(PR_3)$ group, folding back the R substituents as far as they will go, and measuring the angle of the cone that will just contain all the ligands, when the apex of the cone is at the metal. This cone angle and the steric effect increase in the order $P(OMe)_3 < PPh_3 < P(OPh)_3$, therefore, solvation should decrease in the same order, but it is insufficient to justify the sequence for the m^* values.

Among the factors that influence the m^* values the concept of chemical hardness, defined by Chatt *et al.*[44] and first used to explain complex ion formation in water,[45] has not been taken into account. Metal ions are classified as hard or soft according to their preferences for certain ligands. Hard acids will prefer to coordinate to hard bases and soft acids will prefer soft bases; Pd(II) is a soft acid and phosphines and SC_4H_8 are soft bases; moreover, soft acids and soft bases usually form very stable complexes in aqueous solution, and the solvation energy value is a large (negative) number.[46] According to this criterium, the more soft the ligands bound to Pd, the higher the solvation and the lesser the m^* value. Unfortunately, data on absolute hardness for all ligands are not available but, according to Chatt[44] and Pearson,[45,46] the sequence deduced for m^* would also be a reasonable softness sequence. In this way the solvation parameter m^* could, in principle, be related to the hardness of the substituents in metal complexes.

On the other hand, water and ethanol are solvents with low ligating power, and can act only as weak ligands;[41c] they can, in principle, enter the metal coordination sphere upon complex hydrolysis; the increase in rate upon increasing the water content (results not published) can be justified by the increase of solvent permittivity.

These hardness/softness and steric considerations can help to determine which of the two candidates, water or ethanol, is the reactant species. Using data of heats of formation, proton affinities and ionization potentials, Pearson showed that CH_3OH is 1.4 times harder than to H_2O.[46] Despite the lack of hardness data for ethanol, it should be closer to methanol than to water; this feature and the weaker steric effect of water allows one to suggest water as the preferred ligand for Pd^{2+} in its protonated form.



The protonation reaction product [eqn. (10)] is an intermediate of the hydrolysis reaction, since the mechanism involves consecutive reactions (results not published).

Conclusions

Protonation of the orthopalladated C of the organopalladium complex $[Pd(CNN)L]BF_4$ occurs in strongly acidic media; it involves rupture of the organometal bond of the complex and further introduction of water in the metal coordination sphere. The pK_{SH}^{2+} values remain constant with temperature, whereas they noticeably increase with decreasing water content. Vector analysis was shown to be most efficient in the treatment of medium effects. The Hammett acidity function H_0, defined with aniline as a reference base, satisfactorily describes the protonation equilibria over the entire temperature and solvent composition ranges. The excess function X is shown to be adequate only at 25 °C and in 10% ethanol–water. The solvation parameter m^* increases with the hardness of the substituent ligands.

Experimental

The $[Pd(CNN)R]BF_4$ complexes were synthesized as described elsewhere,[47] the other reagents were commercially available. Due to hydrolysis of the cyclometallated complexes, whose constant is around 0.1 s^{-1} at high sulfuric acid concentrations, a modern stopped-flow Bio-Logic SFM-300 spectrophotometer instrument was used. This consists of a mechanical sub-system with three machined syringes, one valve block with 3 × 3-way valves, with the option of including one or two mixers and one aging loop. All SFM syringes, valves, delay lines, and cuvettes are enclosed in a water jacket to allow temperature regulation of the reactant containers. The syringe plungers of the SFM are driven by stepping motors *via* ball screws. The speed capability with all its syringes running gives a dead time below 1 ms in the observation cuvette. The spectral curves were recorded with a high speed Bio-Logic Diode Array DAD spectrophotometer (0.8 ms per spectrum) MMS-UV/1500-1. This procedure drastically reduced the hydrolysis effect at time $t = 0$, where the spectral curves were recorded.

Concentrated sulfuric acid was used to attain the required medium acidity; solutions were prepared by careful addition of the appropriate amounts of commercial H_2SO_4 to a 50 ml bottle containing doubly distilled deionized water, the resulting acidity being determined by titration; this acid solution was put in a syringe. A second syringe contained the complex in pure ethanol, always freshly prepared before each experiment. Proper combination of the amounts of the acid solution and the complex solution enables the required experimental conditions for the kinetic runs. Since the substrate was only sparingly soluble in pure water, to evaluate the solvent effect on the equilibrium constants the experiments were carried out using 10%, 30%, and 50% v:v EtOH–H_2O solvents. The solvent mixtures were prepared at 22 °C. The complex concentrations were always 5×10^{-5} M. The Lambert–Beer law was assessed at all wavelengths used.

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