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THERMAL STUDY OF [Pd(2-Phpy)Cl(L)] COMPLEXES (*L*=PYRIDINES AND AMINES)

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Abstract

The complex $[Pd(2\text{-}Phpy)(\mu\text{-}Cl)]_2$ reacts with pyridines (*L*=pyridine, α-picoline and γ-picoline), amines (*L*=isopropylamine, *tert*-butylamine) and ammonia to form the corresponding *ortho*-palladated derivatives [Pd(2-Phpy)ClL]. The compounds have been characterized by C, H and N analyses and spectroscopic methods (IR and ^{1}H and ^{13}C NMR). TG, DTG and DSC studies of the complexes were carried out in dynamic nitrogen atmosphere. From DSC analyses the heats of decomposition were calculated. The kinetics of the first step of thermal decomposition were evaluated from TG data by isothermal methods for *L*=pyridine and isopropylamine. The activation energies obtained are in the range 90–100 kJ mol^{-1}. The best fitting for data was observed for R2 and A1.5 kinetic models.

Keywords: kinetic analysis, *ortho*-palladated complexes, thermal behaviour

Introduction

Heteroaromatic ligands such as 2-phenylpyridine can easily be *ortho*-metalated by Pd(II) salts *via* C(sp^2)–H bond cleavage [1] usually to give the corresponding acetate or halide-bridged dimers. These dinuclear complexes have been thoroughly studied [2] and employed as precursors of mononuclear cyclometalates of general formula M(C×N)LX (*M*=Pd; *C*×*N*=*ortho*-metalated ligand; *L*=neutral monodentate ligand such as phosphines; *X*=halide) [3–5]. Thermal studies on organometallic compounds of platinum metals group have been reported. In this sense, the thermal behaviour of pentamethyl cyclopentadienylrhodium(III) [6–7], areneruthenium(II) [8] and *ortho*-palladated [9] derivatives has shown the relatively high thermal stability of the chloro-bridged dinuclear precursors.

Here we describe the thermal behaviour of *ortho*-palladated complexes of the type [Pd(C×N)ClL] (*C*×*N*=2-phenylpyridine; *L*=pyridines and amines).

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Experimental

Pyridines, amines and 2-phenylpyridine were obtained from commercial sources and all the solvents were dried by conventional methods before use.

The complex $[Pd(2\text{-}Phpy)(\mu\text{-}Cl]_2$ was prepared according to previously published methods [4].

Preparation of the complexes

The complexes [Pd(2-Phpy)ClL] (*L*=py, α-picoline, γ-picoline; NH_3, isopropylamine, *tert*-butylamine) were obtained by reaction of the dinuclear complex $[Pd(2\text{-}Phpy)(\mu\text{-}Cl]_2$ with the corresponding pyridines and amines in $(CH_3)_2CO$ solution according to the following general method. An excess of neutral ligand (0.65 mmol) was added to a solution of precursor $[Pd(2\text{-}Phpy)(\mu\text{-}Cl)]_2$ (0.162 mmol) in acetone (25 cm^3). When *L*=NH_3 the ligand was added as a 20% aqueous solution. The mixture was then stirred at room temperature for 1 h and the resulting solution was concentrated under reduced pressure to half original volume. The addition of diethyl ether caused the formation of yellow solids, which were filtered off, washed with diethyl ether and air dried.

Characterization

C, H and N analyses were performed with a Carlo Erba microanalyser. Conductivities were measured with a Crison 525 conductimeter. IR spectra were recorded on a Perkin Elmer 16F PC FT-IR spectrophotometer using Nujol mulls between polyethylene sheets. ^{1}H NMR data were recorded on a Bruker AC 200E and ^{13}C NMR data were recorded on a Varian Unity 300 instrument.

[Pd(2-Phpy)Cl(py)]

Yield 70%. Analysis: found (%): C, 51.0; H, 3.3; N, 7.8; calcd.: C, 51.2; H, 3.5; N, 7.5. Non-conductor in acetone. IR (cm^{-1}) (Nujol): 756 (py); 324 (ν PdCl). ^{1}H NMR (δ) (solvent $CDCl_3$; reference $SiMe_4$): 9.40 (d, 1H), 8.90 (d, 2H), 7.79 (m, 2H), 7.60 (d, 1H), 7.41 (m, 3H), 7.10 (m, 2H), 6.87 (m, 1H), 6.14 (d, 1H). ^{13}C NMR (δ) (solvent $CDCl_3$; reference $SiMe_4$): 165.5, 154.8, 153.3 (py), 152.2, 145.7, 138.8 (py), 138.0, 132.5, 129.5, 125.5 (py), 124.8, 123.3, 122.1, 118.3.

[Pd(2-Phpy)(Cl(α-picoline)]

Yield 77%. Analysis: found (%): C, 52.2; H, 3.5; N, 7.0; calcd.: C, 52.5; H, 3.9; N, 7.21. Non-conductor in acetone. IR (cm^{-1}) (Nujol): 774, 756 (α-picoline); 324 (ν PdCl). ^{1}H NMR (δ) (solvent $CDCl_3$; reference $SiMe_4$): 9.40 (d, 1H), 9.92 (d, 1H, α-pic), 7.72 (m, 2H), 7.60 (d, 1H), 7.39 (m, 2H), 7.06 (m, 3H), 6.81 (t, 1H), 5.87 (d, 1H), 3.05 (s, 3H, Me). ^{13}C NMR (δ) (solvent $CDCl_3$; reference $SiMe_4$): 165.4, 160.3 (α-pic), 153.5 (α-pic), 152.4, 151.9 (α-pic), 145.7, 138.7 (α-pic), 137.7, 132.3, 129.5, 126.3 (α-pic), 124.7, 123.3, 122.4, 122.1, 118.2, 27.8 (Me).

[Pd(2-Phpy)(Cl(γ-picoline)]

Yield 75%. Analysis: found (%): C, 52.2; H, 3.4; N, 7.1; calcd.: C, 52.5; H, 3.9; N, 7.2. Non-conductor in acetone. IR (cm^{-1}) (Nujol): 818, 750 (γ-picoline); 326 (ν PdCl). ^{1}H NMR (δ) (solvent $CDCl_3$; reference $SiMe_4$): 9.39 (d, 1H), 8.72 (d, 2H, γ-pic), 7.75 (t, 1H), 7.59 (d, 1H), 7.40 (d, 1H), 7.21 (d, 2H, γ-pic), 7.08 (m, 2H), 6.87 (t, 1H), 6.18 (d, 1H), 2.40 (s, 3H, Me). ^{13}C NMR (δ) (solvent $CDCl_3$; reference $SiMe_4$): 165.5, 154.5, 152.5, 150.1 (γ-pic), 145.7, 138.7 (γ-pic), 132.6, 129.5, 126.4 (γ-pic), 124.7, 123.3, 122.0, 118.2, 30.9 (Me).

[Pd(2-Phpy)(Cl(NH_3)]

Yield 84%. Analysis: found (%): C, 42.2; H, 3.3; N, 8.6; calcd.: C, 42.0; H, 3.5; N, 8.9. Non-conductor in acetone. IR (cm^{-1}) (Nujol): 3310, 3208 (NH_3). ^{1}H NMR (δ) (solvent $CDCl_3$; reference $SiMe_4$): 8.95 (2, 1H), 7.60 (m, 1H), 7.31 (m, 3H), 6.91 (m, 2H), 6.72 (m, 1H), 2.82 (s, 3H, NH_3).

[Pd(2-Phpy)Cl(iPrNH_2)]

Yield 71%. Analysis: found (%): C, 47.4; H, 4.3; N, 7.4; calcd.: C, 47.2; H, 4.8; N, 7.9. Non-conductor in acetone. IR (cm^{-1}) (Nujol): 3268, 3210, 3138 (iPrNH_2). ^{1}H NMR (δ) (solvent $CDCl_3$; reference $SiMe_4$): 9.01 (d, 1H), 7.57 (t, 1H) 7.32 (d, 1H), 7.14 (m, 1H), 6.91 (m, 3H), 6.77 (m, 1H), 3.36 (m, 3H), 1.37 (d, 6H). ^{13}C NMR (δ) (solvent $CDCl_3$; reference $SiMe_4$): 164.5, 152.5, 151.5, 145.8, 138.0, 131.1, 129.0, 124.4, 123.2, 121.9, 117.8, 53.7 (CH-iPr), 32.5 (Me).

[Pd(2-Phpy)Cl(*tert*-BuNH_2)]

Yield 72%. Analysis: found (%): C, 48.4; H, 4.8; N, 7.3; calcd.: C, 48.6; H, 5.1; N, 7.6. Non-conductor in acetone. IR (cm^{-1}) (Nujol): 3270, 3211, (*tert*-BuNH_2). ^{1}H NMR (δ) (solvent $CDCl_3$; reference $SiMe_4$): 9.24 (d, 1H), 7.68 (t, 1H), 7.47 (d, 1H), 7.29 (d, 1H), 6.94 (m, 4H), 3.34 (s, NH_2), 1.44 (s, 9H, Me). ^{13}C NMR (δ) (solvent $CDCl_3$; reference $SiMe_4$): 165.0, 151.7, 151.3, 146.2, 138.4, 132.7, 128.4, 124.5, 123.5, 122.0, 118.0, 53.7 (C-*tert*-Bu), 32.5 (Me).

Thermal analysis

Thermoanalytical data were obtained from TG, DTG and DSC curves. TG and DTG curves were recorded on a Mettler TA-3000 system provided with a Mettler TG-50 thermobalance and DSC curves were recorded on a DSC-20 Mettler instrument. The atmospheres used in different experiments were pure nitrogen (50 cm^3 min^{-1}). The sample mass range was of 4–7 mg.

Table 1 TG and DTG data for the neutral palladium(II) complexes (under dynamic nitrogen atmosphere; heating rate 5°C min^{-1}

Complex	Step	Temperature range/°C	DTG_{max}/ °C	Mass loss/% found(calc.)	Assignment	Enthalpy change/ kJ mol^{-1}
[Pd(2-Phpy)Cl(py)]	1	85–145	137	20.2 (21.1)	py	28.7
	2	286–437	347	45.0 (50.5)	2-Phpy+Cl	
	residue	>440	–	32.2 (28.4)	Pd+C	
[Pd(2-Phpy)Cl(α-pic)]	1	104–167	160	23.3 (23.9)	α-pic	69.7
	2	290–430	351	44.7 (48.8)	2-Phpy+Cl	
	residue	>450	–	29.4 (27.3)	Pd+C	
[Pd(2-Phpy)Cl(γ-pic)]	1	106–173	165	22.9 (23.9)	γ-pic	70.3
	2	284–442	347	44.0 (48.8)	2-Phpy+Cl	
	residue	>450	–	31.7 (27.3)	Pd+C	
[Pd(2-Phpy)Cl(NH_3)]	1	90–165	125	5.2 (5.4)	NH_3	25.4
	2	291–445	337	53.1 (60.6)	2-Phpy+Cl	
	residue	>460	–	38.3 (34.0)	Pd+C	
[Pd(2-Phpy)Cl(iPrNH_2)]	1	90–142	135	16.0 (16.8)	iPr-NH_2	88.4
	2	290–444	335	47.1 (53.4)	2-Phpy+Cl	
	residue	>450	–	33.7 (29.8)	Pd+C	
[Pd(2-Phpy)Cl(*terc*-BuNH_2)]	1	72–127	118	18.7 (19.7)	*terc*-Bu-NH_2	62.6
	2	288–446	347	46.1 (51.5)	2-Phpy+Cl	
	residue	>460	–	32.1 (28.8)	Pd+C	

Results and discussion

Thermal stability

The TG and DSC data of the complexes are summarized in Table 1. All the complexes decompose on heating to give the binuclear complex $[Pd(2\text{-}Phpy)\mu\text{-}Cl)]_2$, according to Eq. (1).

$$[Pd(2\text{-}Phpy)ClL](s) \rightarrow 1/2[Pd(2\text{-}Phpy)(\mu\text{-}Cl)]_2(s)+L(g) \quad (1)$$

where *L*=pyridine, α-picoline, γ-picoline, NH_3, $iPrNH_2$, *tert*-$BuNH_2$

The chloro-bridged binuclear complex could be isolated in every case and identified by IR and ^{1}H-NMR spectroscopy. The enthalpy changes for the first step were measured by integration of the endothermic peaks in the corresponding DSC curves (Table 1). The binuclear intermediates decomposes irregularly between 286 and 446°C.

The complex [Pd(2-Phpy)Cl(py)] loses one pyridine molecule between 85 and 145°C while the complexes with substituted pyridines are more stable: [Pd(2-Phpy)Cl(α-picoline)] and [Pd(2-Phpy)Cl(γ-picoline)] decompose at 104 and 106°C respectively. The enthalpy change for the loss of α-pic and γ-pic is also larger than for pyridine; this fact is in accordance with the stronger donor character of substituted pyridines. The thermal stability of the complex with $iPrNH_2$ is larger than that of the *terc*-$BuNH_2$ derivative in accordance with the values of enthalpy found by DSC (Table 1). In this case, the results suggest that the steric effects are the most important factors in the thermal stability.

Kinetic analysis

Different methods such as linear rising temperature, constant rate thermal analysis [10] or high resolution thermogravimetry [11] have been used in kinetic investigations but the most reliable method for determining kinetic parameters is carefully-controlled isothermal decomposition in which mass loss at a constant temperature is monitored as a function of time [11].

The isothermal TG curves for palladium complexes [Pd(2-Phpy)Cl(py)] and $[Pd(2\text{-}Phpy)Cl(iPrNH_2)]$ at different temperatures are shown in Fig. 1. The delay t_0, preceding the onset of the main reaction usually include contributions of the time required for the sample to attain the reaction temperature. In order to minimize the uncertainty introduced by that time we used the plot α *vs*. $(t–t_0)$ [12].

The differential kinetic equation can be expressed as

$$\frac{d\alpha}{dt} = A e^{-x} f(\alpha) \quad (2)$$

where *A* is a pre-exponential factor for the Arrhenius type rate constant and *x* the reduced apparent activation energy ($x=E_a/RT$). The function $f(\alpha)$ in Eq. (2) is an analytical expression describing the kinetic model of the studied thermal decomposition process.

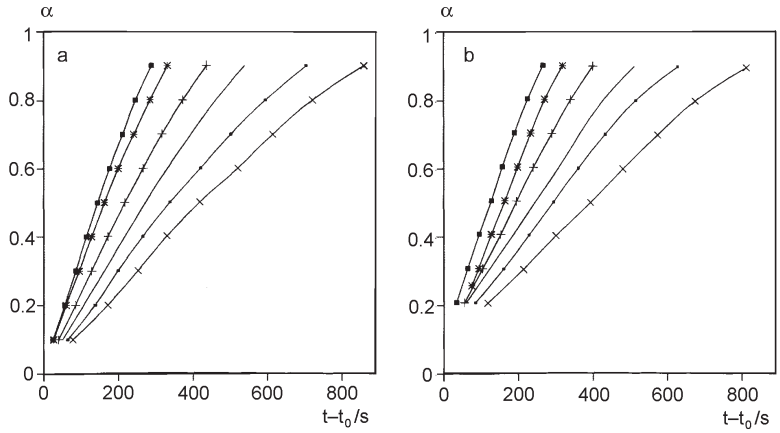

Fig. 1 α *vs*. time plots for the first step of isothermal decomposition of a – [Pd(2-Phpy)Cl(py)] and b – [Pd(2-Phpy)Cl(iPrNH$_2$)]; – × –115°C; – • –118°C; — 121°C; – + – 124°C; – ∗ –127°C; – ■ –130°C

Isoconversional method

By integration of Eq. (2) in isothermal conditions the following equation is obtained:

$$g(\alpha)=Ae^{-x}t \tag{3}$$

The apparent activation energy of the decomposition process in isothermal conditions can be calculated by isoconversional method which follows from logarithmic form of Eq. (3):

$$\ln t=\ln\left(\frac{g(\alpha)}{A}\right)+\frac{E_a}{RT} \tag{4}$$

The slope of ln*t vs*. 1/*T* for the same value of α gives the value of apparent activation energy. This procedure can be repeated for various values of α. The plots of E_a

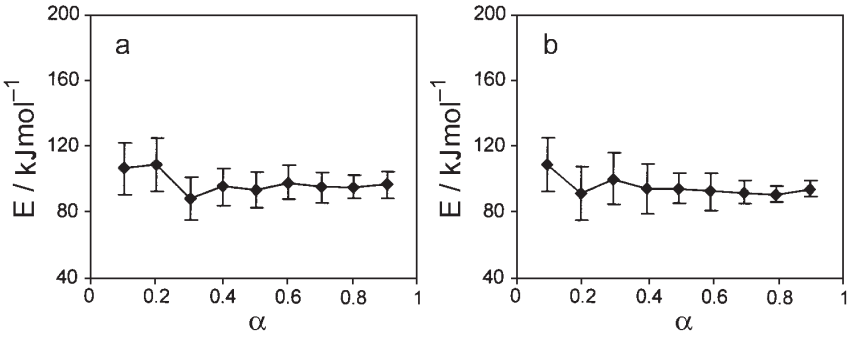

Fig. 2 Plots of apparent activation energy calculated from isothermal TG data by the isoconversional method as a function of α for a – [Pd(2-Phpy)Cl(py)] and b – [Pd(2-Phpy)Cl(iPrNH$_2$)]

as a function of fractional conversion are shown in Fig. 2 within the certain error limits (specified by bars). The average values of apparent activation energy determined in the $0.3<\alpha<0.9$ range are 96±9 and 97±10 for the complexes [Pd(2-Phpy)Cl(py)] and [Pd(2-Phpy)Cl(iPrNH$_2$)] respectively.

Plots of the integrated rate functions, g(α), vs. time

The linearity of the plots of the integrated rate functions, $g(\alpha)$, *vs*. time over the range $0.3\leq\alpha\leq0.9$ was assessed using the correlation coefficient (r). It was difficult to distinguish between applicability of the Am and Rn models. Arrhenius plots constructed using k values from the acceptable $g(\alpha)$ functions gave the apparent activation energies and the pre-exponential factors presented in Table 2. The values of E_a are almost independent of the physical model proposed, a fact which is well established in the literature [13]. Besides, the values of E_a are similar to that found by the isoconversional method.

Table 2 Arrhenius parameters for the isothermal reactions

Models	E_a/kJ mol^{-1}	r	ln(A/s^{-1})
A1.5			
[Pd(2-Phpy)Cl(py)]	97±6	0.9969	22.8±1.8
[Pd(2-Phpy)Cl(iPrNH$_2$)]	94±9	0.9989	23.5±2.1
A2			
[Pd(2-Phpy)Cl(py)]	98±7	0.9946	22.4±2.0
[Pd(2-Phpy)Cl(iPrNH$_2$)]	94±8	0.9970	23.4±1.9
A3			
[Pd(2-Phpy)Cl(py)]	99±9	0.9945	22.0±1.6
[Pd(2-Phpy)Cl(iPrNH$_2$)]	95±8	0.9981	22.9±2.1
R2			
[Pd(2-Phpy)Cl(py)]	98±9	0.9961	22.3±1.8
[Pd(2-Phpy)Cl(iPrNH$_2$)]	95±7	0.9980	22.4±1.7
R3			
[Pd(2-Phpy)Cl(py)]	98±8	0.9974	22.0±2.5
[Pd(2-Phpy)Cl(iPrNH$_2$)]	94±7	0.9971	22.3±1.9

Reduced-time plots

For an isokinetic process, if the times required to attain a set value of α (e.g., α=0.5) at different (isothermal) temperatures are determined ($t_{0.5}$), then plots of α *vs*. reduced time ($t_{red}=t/t_{0.5}$) can be prepared [14]. This method consists in comparing the experimental data (in the form of reduced time) with the well-known calculated data for the models in Table 2. As can be seen from Fig. 3, the best fits of the experimental results is for A1.5 and R2 models.

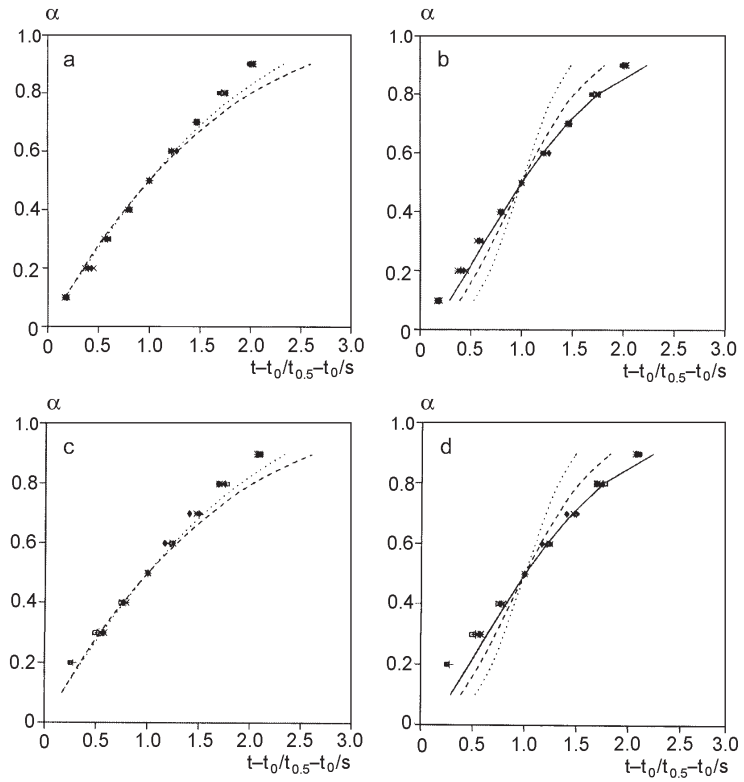

Fig. 3 Plots of reduced-time for a – [Pd(2-Phpy)Cl(py)] ··· R2; --- R3; b – [Pd(2-Phpy)Cl(py)] --A2; ··· A3; — A1.5; c – [Pd(2-Phpy)Cl(iPrNH$_2$)]) ··· R2; --- R3; and d – [Pd(2-Phpy)Cl(iPrNH$_2$)]) --A2; ··· A3; — A1.5; *T*= – × –115°C; – ◆ –118°C; – · – 121°C; – + –124°C; – ∗ –127°C; – □ –130°C

Method of Hancock–Sharp

In order to discriminate between models R2 and A1.5 we used the method of Hancock–Sharp [15] based in the following equation:

$$\ln[-\ln(1-\alpha)]=n\ln t+B \tag{5}$$

The plotting of $\ln[-\ln(1-\alpha)]$ *vs*. $\ln t$ for α values ranging from 0.05 to 0.65 allows the *n* parameter to be determined. This parameter is characteristic of the reaction mechanism [16], being n=1.09 and n=1.5 for R2 and A1.5 mechanisms respectively.

The results of the above plot are presented in Table 3, the found values for *n* parameter are closer to 1.09, so we can conclude that R2 is the most probable reaction mechanism.

Table 3 Hancock–Sharp parameters for the isothermal reactions

[Pd(2-Phpy)Cl(py]		*T*/°C	[Pd(2-Phpy)Cl(iPrNH$_2$)]	
n	*r*		*n*	*r*
1.16±0.07	0.99376	115	1.14±0.06	0.99699
1.16±0.05	0.99670	118	1.15±0.03	0.99968
1.15±0.04	0.99750	121	1.12±0.03	0.99945
1.14±0.04	0.99748	124	1.14±0.09	0.99418
1.07±0.04	0.99674	127	1.20±0.05	0.99926
1.10±0.05	0.99605	130	1.03±0.07	0.99580

Conclusions

The results presented above show that the thermal stability of complexes [Pd(2-Phpy)Cl(L)] with substituted pyridines (*L*=α-picoline, γ-picoline) is higher than that of the complex with pyridine. On the other hand, the complex with iPrNH$_2$ shows a larger thermal stability than that with *tert*-BuNH$_2$.

With regard to the kinetic of the first step of thermal decomposition we found for the complexes with *L*=pyridine, iPrNH$_2$ similar values of activation energies (in the range 90–100 kJ mol^{-1}) and the models that best fit for data are R2 and A1.5 in both cases. It can be established by the Hancock–Sharp method that R2 is the most probable mechanism.

The release of ligand yields the same product, [Pd(2-Phpy)(μ-Cl)]$_2$, in all the cases. This compound shows a relatively high thermal stability, this fact probably is related with the similar values of E_a found for the two complexes studied in the present work.

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