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# Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry

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# Palladium(II) Complexes Containing 2,6-Bis(Imino)Pyridines: Synthesis, Characterization, Thermal Study, and Catalytic Activity in Suzuki Reactions

## Osman Dayan,<sup>1</sup> Fatih Doğan,<sup>1</sup> İsmet Kaya,<sup>1</sup> and Bekir Çetinkaya<sup>2</sup>

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A series of palladium complexes: [(Pydim)PdCl](PdCl<sub>3</sub>) (Pydim (1): pyridine-2,6-diimine) have been synthesized from palladium dichloride and the corresponding pydim. The Pd (II) complexes have been used as catalyst in the Suzuki reaction of aryl halides. Moreover, thermal behaviors of palladium complexes have been studied in nitrogen atmosphere using TG/DTG and DTA techniques. The values of activation energy Ea, and reaction order n, the entropy change  $\Delta S^*$ , enthalpy change  $\Delta H^{\#}$ , and Gibbs free energy change  $\Delta G^{\#}$  of the thermal decomposition were calculated by means of several methods based on the single heating rate.

Keywords activation energy, Pd(II) complexes, pyridine-2,6diimines, Suzuki reaction, thermal behavior

#### INTRODUCTION

Transition metal complexes with tridentate nitrogen donor ligands containing pyridine-ring (**I-IV**) have been extensively synthesized and studied for many potential applications.<sup>[1-4]</sup> For example, these complexes as catalysts have been widely used in various organic transformation reactions, especially polymerization, epoxidation, and hydrogenation reactions.<sup>[5-7]</sup>

On the other hand, the most powerful method for the preparation of biaryl compounds is Suzuki reactions involving crosscoupling of aryl halides with aryl boronic acids.<sup>[8–11]</sup> Suzuki reactions involve the use of various Pd complexes as catalyst in various solvents. These complexes include many different kinds of nitrogene-based palladium complexes. However, palladium complexes containing planar tridentate pyridine-bridged N,N',N



ligands are rare in literature. More recently, two related papers on the catalytic activity of pyridine-2,6-dimines (**IV**)/Palladium complexes in the Suzuki reactions of aryl halides and phenylboronic acid were published.<sup>[12,13]</sup>

On the other hand, the non-isothermal thermogravimetry (TG) with a linear temperature growth is a method frequently used to characterize materials from their thermal behavior standpoint. In addition, it enables us to determine apparent kinetic parameters of heterogeneous reactions (the reaction order *n*, the activation energy *E*, and the frequency factor *A*). For instance, Doğan et al.<sup>[14–16]</sup> investigated using thermo gravimetric technique on the effect of the calculation methods on the solid state decomposition kinetic of semiconducting polymeric materials. Also, Doğan et al.<sup>[17]</sup> have investigated the thermal behavior, kinetic and thermodynamic parameters of imidazolinium and benzimidazolium bromide salts with pentafluorobenzyl substitutients in a nitrogen atmosphere with TG/DTG and DTA. Kok <sup>[18]</sup> estimated the thermal analysis and kinetics of several coal and oil shale samples by using the same method based on the single heating rate. A similar study using isothermal function by various methods on Ruthenium (II)

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complexes containing pyridine-2,6-diimines<sup>[19]</sup> and rhodium(III)-pentamethylcyclopentadienyl and ruthenium(II)-arene has been reported.<sup>[20]</sup>

In this work, we prepare well-defined Pd(II) catalyst precursors incorporating pydim ligands for the Suzuki reactions, described the thermal behaviors of those, and determined the kinetic and thermodynamic parameters such as the reaction order *n*, activation energy  $E_a$ , the entropy change  $\Delta S^{\#}$ , enthalpy change  $\Delta H^{\#}$ , and Gibbs free energy change  $\Delta G^{\#}$  of the thermal decomposition by means of MC, vK, MKN and WYHC methods.

#### **EXPERIMENTAL**

All manipulations were performed under argon atmosphere using standard Schlenk techniques. All reagents were obtained from commercial suppliers and used without further purification. Solvents were dried by standard methods and distilled under argon before use. 1a,<sup>[21]</sup> 1b,<sup>[22]</sup> 1c,<sup>[23]</sup> 1d and 1e<sup>[6]</sup> and 1f<sup>[24]</sup> were synthesized according to published procedures. NMR spectra were recorded at 297 K on a Varian Mercury AS 400 NMR spectrometer at 400 MHz ( $^{1}$ H), 100,56 MHz ( $^{13}$ C). The C, H and N analyses were performed using a CHNS-932 (LECO) instrument at Inonu University Scientific and Technological Research Center, IBTAM. Infrared spectra were measured with a Perkin Elmer SpectrumOne FTIR system and recorded using a universal ATR sampling accessory within the range 550-4000 cm-1. GC measurements for catalytic experiments were performed using an Agillent 6890N GC instrument with a HP5 capillary column. The DTA and TG curves were obtained with TG-DTA Perkin Elmer Diamond system apparatus. The measurements were performed by using a dynamic nitrogen atmosphere at a flow rate of 200 mL.min<sup>-1</sup> up to 1000°C. The heating rate was 10°C min<sup>-1</sup>, and the sample sizes ranged in mass from 8 to 10 mg contained in platinum crucible. All the experiments were performed twice for repeatability and the results showed good reproducibility with the smaller variations in the kinetic parameters.  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> is used as a reference material.

# Ligands and Complexes, General Synthesis Procedures (1a-F and 2a-F)

**1a-f** were synthesized according to published procedures.<sup>[6,21-24]</sup> **2a** was described in another publication.<sup>[13]</sup> **2a-f** were prepared a modification of literature method:<sup>[12]</sup> An ethanolic solution (20 mL) of 1.10 eq. of **1** was mixed with PdCl<sub>2</sub> (0.177 g, 1 mmol). The reaction mixture was heated under reflux for 10 h. The precipitate occurred in reaction mixture. The reaction mixture was cooled and filtered. The precipitate was washed with diethyl ether (3 × 10 mL) and pentane (3 × 10 mL), respectively. The desired products were dried under reduced pressure at 50°C for 1 h.

#### Synthesis of Complex 2a

Yield: 0.29 g, % 86. Anal. calcd. for  $C_{21}H_{19}Cl_4N_3Pd_2$ : C: 37.76; H: 2.87; N: 6.29; found: C: 40.91; H: 3.41; N: 6.59. <sup>1</sup>H-NMR ( $\delta$ , d6-DMSO): 2.54 (s, 6 H, N=C-Me), 7.20 (t, J = 8.0Hz, 2 H, Ph- $H_p$ ), 7.32 (m, 4 H, Ph- $H_m$ ), 7.51 (d, J = 8.0 Hz, 4 H, Ph- $H_o$ ), 8.57 (d, J = 7.8 Hz, 2 H, Py- $H_m$ ), 8.75 (t, J = 8.0 Hz, 1 H, Py- $H_p$ ). <sup>13</sup>C-NMR ( $\delta$ , d6-DMSO): 26.1, 123.5, 125.3, 129.6, 139.7, 142.8, 152.9, 155.9, 184.6. IR (cm<sup>-1</sup>): 1634 ( $\nu_{C=N}$ ).

#### Synthesis of Complex 2b

Yield: 0.318 g, % 90. Anal. calcd. for  $C_{21}H_{17}Cl_4F_2N_3Pd_2$ : C: 35.83; H: 2.43; N: 5.97; found: C: 38.80; H: 4.00; N: 6,63%. <sup>1</sup>H-NMR ( $\delta$ , *d*6-DMSO): 2.50 (s, 6 H, N=C-*Me*), 7.26–7.34 (m, 8 H, Ph-*H*), 8.50 (d, *J* = 8.0 Hz, 2 H, Py-*H<sub>m</sub>*), 8.69(t, *J* = 8.0 Hz, 1 H, Py-*H<sub>p</sub>*). <sup>13</sup>C-NMR ( $\delta$ , *d*6-DMSO): 23.3, 123.8, 126.1, 130.6, 133.5, 140.6, 156.7, 163.9, 172.4. IR (cm<sup>-1</sup>): 1614 ( $\nu_{C=N}$ ).

#### Synthesis of Complex 2c

Yield: 0.306 g, % 81. Anal. calcd. for  $C_{25}H_{29}Cl_4N_5Pd_2$ : C: 39.81; H: 3.88; N: 9.29; found: C: 43.97; H: 4.59; N: 9.81%. <sup>1</sup>H-NMR ( $\delta$ , d6-DMSO): 2.47 (s, 6 H, N=C-Me), 2.93 (m, 12 H, 4-N(Me)<sub>2</sub>-Ph), 6.67 (d, J = 7.8 Hz, 4 H, Ph- $H_o$ ), 7.05 (d, J = 7.8 Hz, 4 H, Ph- $H_m$ ), 8.33 (d, J = 8.0 Hz, 2 H, Py- $H_m$ ), 8.53 (t, J = 8.0 Hz, 1 H, Py- $H_p$ ). <sup>13</sup>C-NMR ( $\delta$ , DMSO): 21.3, 43.2, 122.6, 123.3, 131.1, 134.6, 138.8, 146.5, 154.1, 160.4. IR (cm<sup>-1</sup>): 1603 ( $\nu_{C=N}$ ).

#### Synthesis of Complex 2d

Yield: 0.313 g, %80. Anal. calcd. for C<sub>29</sub>H<sub>35</sub>Cl<sub>4</sub>N<sub>3</sub>Pd<sub>2</sub>: C: 44.64; H: 4.52; N: 5.39; found: C: 46.17; H: 5.66; N: 5.58%. <sup>1</sup>H-NMR ( $\delta$ , *d*6-DMSO): 1.27 (s, 18 H, -C(*CH*<sub>3</sub>)<sub>3</sub>), 2.44 (s, 6 H, N=C-*Me*), 7.13 (d, *J* = 8.6 Hz, 4 H, Ph-*H*<sub>o</sub>), 7.45 (d, *J* = 8.6 Hz, 4 H, Ph-*H*<sub>m</sub>), 8.46 (d, *J* = 8.2 Hz, 2 H, Py-*H*<sub>m</sub>), 8.65 (t, *J* = 8.2 Hz, 1 H, Py-*H*<sub>p</sub>). <sup>13</sup>C-NMR ( $\delta$ , *d*6-DMSO): 19.2, 25.3, 31.1, 34.2, 122.3, 125.5, 138.9, 142.2, 147.0, 150.5, 152.2, 163.6. IR (cm<sup>-1</sup>): 1626 ( $\nu$ <sub>C=N</sub>).

#### Synthesis of Complex 2e

Yield: 0.337 g, % 93. Anal. calcd. for  $C_{25}H_{27}Cl_4N_3Pd_2$ : C: 43.46; H: 3.76; N: 5.80; found: C: 45.87; H: 4.73; N: 6.55%. <sup>1</sup>H-NMR ( $\delta$ , d6-DMSO): 2.31 (s, 12 H, 3,5-(Me)\_2-Ph), 2.44 (s, 6H, N=C-Me), 7.14 (s, 2H, Ph- $H_p$ ), 7.81 (m, 4 H, Ph- $H_o$ ), 8.64 (d, J = 8.0 Hz, 2H, Py- $H_m$ ), 8.81 (t, J = 8.0Hz, 1 H, Py- $H_p$ ). <sup>13</sup>C-NMR ( $\delta$ , d6-DMSO): 16.8, 22.9, 120.5, 124.3, 128.1, 131.2, 144.3, 153.1, 156.9, 161.4. IR (cm<sup>-1</sup>): 1627 ( $\nu_{C=N}$ ).



SCH. 1. Synthesis of Pydim ligands.

#### Synthesis of Complex 2f

Yield: 0.354 g, % 80. Anal. calcd. for  $C_{27}H_{31}Cl_4N_3Pd_2$ : C: 43.11; H: 4.15; N: 5.59; found: C: 45.63; H: 5.49; N: 5.98%. <sup>1</sup>H-NMR ( $\delta$ , *d*6-DMSO): 2.21 (s, 12 H, 2,6-(*Me*)<sub>2</sub>,4-Me-Ph), 2.22 (s, 6 H, 2,6-(Me)<sub>2</sub>,4-*Me*-Ph), 3.36 (s, 6 H, N=C-*Me*), 6.93 (s, 4 H, Ph-*H*), 8.59 (d, J = 8.2 Hz, 2 H, Py-*H<sub>m</sub>*), 8.77 (t, J = 8.2 Hz, 1 H, Py-*H<sub>p</sub>*). <sup>13</sup>C-NMR ( $\delta$ , *d*6-DMSO): 17.6, 20.9, 23.5, 126.4, 29.8, 133.6, 138.7, 141.4, 142.3, 153.15, 164.9. IR (cm<sup>-1</sup>): 1631 ( $\nu_{C=N}$ ).

#### Suzuki Cross-Coupling Reactions: General Procedure

In a typical reaction, the catalyst (1 mmol % of Pd complexes), aryl halides (1.0 mmol), phenyl boronic acid (1.5 mmol),  $Cs_2CO_3$  (2.0 mmol), diethyleneglycol-di-n-buthylether as internal standard (30 mg), 2-propanol (3 mL) were all added to a small Schlenk tube and the mixture was heated at 80°C for 1 h under argon. At the end, the mixture was cooled, filtrated and concentrated. The purity of the compounds was checked by GC and yields were based on aryl halides.

#### **RESULTS AND DISCUSSION**

#### Synthesis of Ligands and Complexes

Pydim ligands (**1a-f**) were prepared in good yields by a Schiff-base condensation reaction (Scheme 1). The preparations of Pydims have been described elsewhere.<sup>[6,21–24]</sup> All compounds were characterized by NMR and FT-IR techniques. Py- $H_p$  and Py– $H_m$  protons for these compounds were observed as doublets and triplets in a 2:1 ratio at 7.82–8.48 ppm. On the other hand, PdCl<sub>2</sub> reacts with 1.0 equiv. of pydim ligands (**1**) in refluxing EtOH and the resulting air-stable four coordinated

complexes can be isolated (Scheme 2). All of the complexes were soluble in dimethylsulfoxide and were fully characterized by elemental analysis and spectroscopic methods.

The <sup>1</sup>H-NMR spectra of these complexes showed some differences from their respective ligands, especially in the pyridine backbone. Py- $H_p$  and Py- $H_m$  protons for all Pydim-Pd(II) (**2af**) complexes were observed as triplets and doublets in a 1: 2 ratio, which had shifted towards downfield when compared to their respective free ligands (**1a-f**) (Table 1).

The IR spectra of **1a-f** showed peaks  $\nu$ (C=N) around 1655–1621 cm<sup>-1</sup> given in Table 2. Upon the coordination of Pd(II), C=N peaks are shifted significantly to lower frequency.

#### **Catalytic Studies**

Studies of the Suzuki reaction in 2-propanol catalyzed by the **2a-f** complexes were carried out under identical conditions to allow comparison of results.

Preliminary studies were performed using **2a** as a catalyst as this complex was reported in Suzuki reaction in H<sub>2</sub>O at 80°C.<sup>[13]</sup> As a result, all complexes were found to be active catalysts in Suzuki reaction, leading to the formation of biaryl compounds with moderate to good conversions (21–97%) after 1h. The results are summarized in Table 3.

The most remarkable features are (i) very rapid reactions achieved at  $80^{\circ}$ C. The reactions become notably slower as the temperature decreases. (ii) Reaction rate strongly depended on the amount of catalyst, which should not be lower than 1%. Otherwise, the reaction becomes slower. (iii) The efficiency of the catalyst seems to depend on the imine fragment of the pydim ligands. And (iv) although all of the Pydim-Pd(II) complexes are active catalysts, **2f** is much more efficient. Catalytic activity



SCH. 2. Synthesis of Pd(II) complexes.

	<sup>1</sup> H-NMF	R (δ, ppm)		
Compounds	Py-Hp	Py-Hm		
1a	7.91	8.40	F	Ру-Нр
2a	8.75	8.57	ſ	Py-Hm
1b	7.87	8.34		
2b	8.69	8.50		
1c	7.82	8.32	Δr <sup>−</sup> N→	Pd - N_Ar
2c	8.53	8.33		
1d	7.86	8.36		
2d	8.65	8.46	Ar:	
1e	7.84	8.31		
2e	8.81	8.64	a)	b) — г
1f	7.90	8.48		
2f	8.77	8.59		
			c)N	d)
			e) –	f)

 TABLE 1

 Selected <sup>1</sup>H-NMR resonances of the synthesized compounds 1 and 2

increases when electron donating groups are introduced at the aryl ring.

#### **Thermal Stability**

Pydim-Palladium(II) complexes (**2a-f**) were studied by thermogravimetric analysis from ambient temperature to  $1000^{\circ}$ C in nitrogen atmosphere. Typical TG/DTG and DTA curves for compounds in the nitrogen atmosphere are present in Figures 1, 2 and 3. The initial and final temperatures and total mass loses for each decomposition step in the thermal decomposition of complexes are given Table 4, together with temperatures of greatest rate of decomposition (DTG<sub>max</sub>), evolved moiety and the theoretical percentage mass losses.

TABLE 2 Selected IR bands ( $\nu$ C=N cm<sup>-1</sup>) of the synthesized compounds 1 and 2

		Compounds						
	a	b	c	d	e	f		
1 2	1655 1634	1621 1614	1622 1603	1633 1626	1636 1627	1643 1631		

#### **Kinetic Parameters**

The four methods investigated in this paper are those by vK, MC, MKN and WHYC.

The Madhusudanan-Krishnan-Ninan method<sup>[25]</sup>

$$\ln\left[\frac{g(\alpha)}{T^{1.9206}}\right] = \ln\left(\frac{AE}{\beta R}\right) + 3.7678 - 1.9206\ln E - 0.12040(\frac{E}{T})$$
[1]

The MacCallum-Tanner method<sup>[26]</sup>

$$\log g(\alpha) = \log \left(\frac{AE}{\beta R}\right) - 0.4828E^{0.4351} - \left(\frac{0.449 + 0.217E}{10^{-3}T}\right)$$
[2]

Wanjun-Yuwen-Hen-Cunxin method<sup>[27]</sup>

$$\ln\left[\frac{g(\alpha)}{T^{1.8946}}\right] = \left[\ln\frac{AR}{\beta E} + 3.6350 - 1.8946\ln E\right] - 1.0014\left(\frac{E}{RT}\right)$$
[3]

The van Krevelen method<sup>[28]</sup>

$$\ln g(\alpha) = \ln \left[ \frac{A(0.368/T_m)^{\frac{E_a}{RT_m}}}{\beta \left(\frac{E_a}{RT_m} + 1\right)} \right] + \left(\frac{E_a}{RT_m} + 1\right) \ln T \quad [4]$$

	}— B(OH) <sub>2</sub> + X−		COMe cat.
Entry	Complex	Х	Yield
1	2a	Br	65
2	2b	Br	59
3	2c	Br	78
4	2d	Br	72
5	2e	Br	67
6	<b>2f</b>	Br	97 (23) <sup>b</sup> (34) <sup>c</sup>
7	2a	Cl	35
8	2b	Cl	21
9	2c	Cl	46
10	2d	Cl	43
11	2e	Cl	39
12	2f	Cl	56

 TABLE 3

 Suzuki reaction of phenylboronic acid with aryl halides<sup>a</sup>

<sup>*a*</sup>Reaction conditions: 1 mmol of halide substrate, 1.5 mmol of PhB(OH)<sub>2</sub>, 2.0 mmol of Cs<sub>2</sub>CO<sub>3</sub> as base, 1 mol % of catalyst, 3 mL of 2-propanol, 80 °C, GC yield. <sup>*b*</sup> Reaction conditions: 1 mmol of halide substrate, 1.5 mmol of PhB(OH)<sub>2</sub>, 2.0 mmol of Cs<sub>2</sub>CO<sub>3</sub> as base, 0.1 mol % of catalyst, 3 mL of 2-propanol, 80°C, GC yield. <sup>*c*</sup> Reaction conditions: 1 mmol of halide substrate, 1.5 mmol of Cs<sub>2</sub>CO<sub>3</sub> as base, 1 mol % of catalyst, 3 mL of 2-propanol, 80°C, GC yield. <sup>*c*</sup> Reaction conditions: 1 mmol of halide substrate, 1.5 mmol of Cs<sub>2</sub>CO<sub>3</sub> as base, 1 mol % of catalyst, 3 mL of 2-propanol, 80°C, GC yield. <sup>*c*</sup> Reaction conditions: 1 mmol of halide substrate, 1.5 mmol of Cs<sub>2</sub>CO<sub>3</sub> as base, 1 mol % of catalyst, 3 mL of 2-propanol, 25°C, GC yield.

In the equations above,  $\alpha$ ,  $g(\alpha)$ ,  $\beta$ ,  $T_m$ , E, A, R are the degree of reaction, integral function of conversion, heating rate, DTG peak temperature, activation energy (kJ.mol<sup>-1</sup>), pre-exponential factor (min<sup>-1</sup>) and gas constant (8.314 J.mol<sup>-1</sup>K<sup>-1</sup>), respectively.

In this study, the several methods based on a single heating rate were used in the thermal analysis. The linearization curves of the each decomposition step of the complexes were obtained using the least squares method. From the TG/DTG and DTA curves, the reaction order, n and activation energy, E of the decomposition have been elucidated by the first one of the methods mentioned above which has higher linear regression coefficient obtained for Arrhenius plots (Table 5). The kinetic and thermodynamic parameters related to the complexes were calculated by the software developed in our laboratory using PHP Web programming language.<sup>[29]</sup>



FIG. 1. Typical TG curves for 2a-f in the nitrogen atmosphere.



FIG. 2. Typical DTG curves for 2a-f in the nitrogen atmosphere.

The decomposition processes of Pd(II)-pydim complexes are similar for **2a-b**, **2c-e** and **2f**. However the thermal decomposition pattern of each complex shows a different decomposition pattern due to the different aryl groups.

From the TG curve for complex **2a**, it appears that the sample decomposes in two stages over the temperature range  $30-579^{\circ}$ C. The first decomposition occurs between 30 and  $106^{\circ}$ C with a mass loss 6.99% in mass due to the loss of 1/2 molecule Cl<sub>2</sub>. This step required activation energy of 39.87 kJ.mol<sup>-1</sup> with the order of 0.7 according to MC method. In the second decomposition step, a mass loss of 45.98% with the order of 1.5 and 46.26 kJ.mol<sup>-1</sup> activation energy according to MC involved the elimination of 3 molecules C<sub>6</sub>H<sub>5</sub> on the complex in temperature range 106–579°C. **2b** is more stable than **2a** and decompose at 101 and 193°C, respectively, to give 1/2 molecule Cl<sub>2</sub> and 2

molecule  $C_6H_4F_2$  from the **2b**. The reaction order and activation energies for the first and second decomposition steps of **2b** were found to be 1.6 and 218.8 kJ.mol<sup>-1</sup>, and 2.6 and 97.87 kJ.mol<sup>-1</sup>, respectively, according to vK method and MKN method. **2f** exhibited two step decomposition processes. In the first step, 1/2 molecule  $Cl_2$  was eliminated in the temperature range 120– 195°C with a 6.44% mass loss. This reaction was in an order of 1.5 with an activation energy of 165.5 kJ.mol<sup>-1</sup>according to vK method. The second decomposition step occurs in the temperature range 195–565°C with 42.6% mass loss and corresponds to the formation of 2 molecules  $C_9H_{11}$  on the complex. As seen in Figure3, from the DTA profile two exothermic peaks for **2a** and **2f** are noted. The maximas of these peaks, which are due to the formation of intermediate, are found to be 75 and 257, 149 and 244°C, respectively. One exothermic peaks



FIG. 3. Typical DTA curves for 2a-f.

DTA<sub>max</sub>/°C DTG<sub>max</sub>/°C Temperature range /°C DTA Weight loss /%, found (calc.) Complexes Step Assignment 2a Ι 75 65 30-106 Exo 6.99 (7.24) 1/2 Cl<sub>2</sub> Π 257 247 106-579 45.98 (45.03) Exo  $3 C_6 H_5$ residue >579 2b 146 101-182 7.14 (6.74) 1/2 Cl<sub>2</sub> Ι Π 219 235 193-625 Exo 36.28 (36.12)  $2C_6H_4F_2$ residue >625 Ι 261 245 109-498 41.03 (41.66) 2C8H10N 2c Exo residue >489 134-699 51.12 (49.33) 1/2 Cl<sub>2</sub>, 2C<sub>10</sub>H<sub>13</sub> 2d Ι 269 263 Exo >699 residue 2e Ι 286 270 234-336 Exo 56.97 (57.60)  $3C_8H_9$ residue >336 2f Ι 149 159 120-195 6.44 (6.18) 1/2 Cl<sub>2</sub> Exo Π 244 261 195-565 42.62 (41.46) 2C9H11 Exo residue >565

TABLE 4TG/DTG and DTA data for the **2a-f** 

for 2b is noted. The maximum of this peak is found to be  $219^{\circ}$ C.

From TG curves (Figure 1), **2c-e** exhibited one step decomposition process. Also, exothermic thermal effect at 261, 269, and 286°C in DTA profiles correspond to the decomposition of **2c, 2d,** and **2e** complexes, respectively. The reaction orders and

activation energies for **2c-e** complexes were found to be 1.30 and 47.35 kJ.mol<sup>-1</sup> according to vK method, and 1.60 and 59.38 kJ.mol<sup>-1</sup>, 2.5 and 317.3 kJ.mol<sup>-1</sup> according to MC method, respectively.

The kinetic data obtained by different methods agree with each other. The thermal stabilities of complexes increase in the

Kinetic data on complexes"								
Step	Methods	n	$E_a$	lnA	$\Delta S^{\#}$	$\Delta H^{\!\#}$	$\Delta G^{\#}$	r
Ι	MC	0.7	39.87	17.82	-97.760	37.05	70.103	0.99904
	vK	0.7	36.81	17.07	-104.00	33.99	69.152	0.99902
II	MC	1.5	46.26	15.47	-120.88	43.98	106.84	0.99962
	vK	1.9	41.94	14.86	-125.93	47.66	113.12	0.99952
Ι	vK	1.6	218.8	88.27	486.28	225.37	21.627	0.99905
	MC	1.5	217.6	65.76	299.07	214.20	88.894	0.99885
II	MKN	2.6	97.87	20.77	-76.62	93.54	132.47	0.99962
	WHYC	2.6	97.77	20.69	-77.26	93.54	132.79	0.99962
Ι	vK	1.3	47.35	13.01	-141.35	43.04	116.26	0.99948
	MC	1.1	47.07	14.58	-128.30	42.76	109.22	0.99890
Ι	MC	1.6	59.38	15.39	-121.85	44.92	110.23	0.99681
	vK	2.2	56.77	15.68	-119.39	52.31	116.31	0.99645
Ι	MC	2.5	317.3	74.83	372.38	312.85	110.65	0.99972
	vK	2.7	319.4	68.06	316.06	324.94	153.32	0.99972
Ι	vK	1.5	165.56	67.02	309.29	171.964	38.350	0.99813
	MC	1.4	169.52	75.94	383.46	165.924	0.2697	0.99745
II	MC	2.1	65.34	18.91	-92.515	60.900	110.30	0.99825
	MKN	2.2	58.52	10.85	-159.53	54.080	139.27	0.99735
	Step I II I I I I I I I I	Step         Methods           I         MC           vK         WK           II         WK           I         vK           I         VK           I         VK           I         VK           I         VK           I         WHYC           I         VK           MC         MC           I         MC	Step         Methods         n           I         MC         0.7           VK         0.7           II         MC         1.5           VK         1.9           I         VK         1.6           MC         1.5           II         MKN         2.6           I         VK         1.3           MC         1.1           I         MC         1.6           VK         2.2         I           I         VK         2.2           I         MC         1.6           VK         2.2         I           I         VK         2.7           I         VK         1.5           MC         1.4           II         MC         2.1	Step         Methods         n         Ea           I         MC         0.7         39.87           vK         0.7         36.81           II         MC         1.5         46.26           vK         1.9         41.94           I         vK         1.6         218.8           MC         1.5         217.6           II         MKN         2.6         97.87           WHYC         2.6         97.77           I         vK         1.3         47.35           MC         1.1         47.07           I         wK         2.2         56.77           I         MC         1.6         59.38           vK         2.2         56.77           I         MC         2.5         317.3           vK         2.7         319.4           I         vK         1.5         165.56           MC         1.4         169.52           II         MC         2.1         65.34           MKN         2.2         58.52	StepMethods $n$ $E_a$ $\ln A$ IMC0.739.8717.82vK0.736.8117.07IIMC1.546.2615.47vK1.941.9414.86IvK1.6218.888.27MC1.5217.665.76IIMKN2.697.8720.77WHYC2.697.7720.69IvK1.347.3513.01MC1.147.0714.58IMC1.659.3815.39vK2.256.7715.68IMC1.5165.5667.02MC1.4169.5275.94IIMC2.165.3418.91MKN2.258.5210.85	StepMethods $n$ $E_a$ $\ln A$ $\Delta S^{\#}$ IMC0.739.8717.82 $-97.760$ vK0.736.8117.07 $-104.00$ IIMC1.546.2615.47 $-120.88$ vK1.941.9414.86 $-125.93$ IvK1.6218.888.27486.28MC1.5217.665.76299.07IIMKN2.697.8720.77 $-76.62$ WHYC2.697.7720.69 $-77.26$ IvK1.347.3513.01 $-141.35$ MC1.147.0714.58 $-128.30$ IMC1.659.3815.39 $-121.85$ vK2.256.7715.68 $-119.39$ IMC2.5317.374.83372.38vK2.7319.468.06316.06IvK1.5165.5667.02309.29MC1.4169.5275.94383.46IIMC2.165.3418.91 $-92.515$ MKN2.258.5210.85 $-159.53$	StepMethods $n$ $E_a$ $\ln A$ $\Delta S^{\#}$ $\Delta H^{\#}$ IMC0.739.8717.82 $-97.760$ 37.05vK0.736.8117.07 $-104.00$ 33.99IIMC1.546.2615.47 $-120.88$ 43.98vK1.941.9414.86 $-125.93$ 47.66IvK1.6218.888.27486.28225.37MC1.5217.665.76299.07214.20IIMKN2.697.8720.77 $-76.62$ 93.54WHYC2.697.7720.69 $-77.26$ 93.54IvK1.347.3513.01 $-141.35$ 43.04MC1.147.0714.58 $-128.30$ 42.76IMC1.659.3815.39 $-121.85$ 44.92vK2.256.7715.68 $-119.39$ 52.31IMC1.5165.5667.02309.29171.964MC1.4169.5275.94383.46165.924IIMC2.165.3418.91 $-92.515$ 60.900MKN2.258.5210.85 $-159.53$ 54.080	StepMethods $n$ $E_a$ $\ln A$ $\Delta S^{\#}$ $\Delta H^{\#}$ $\Delta G^{\#}$ IMC0.739.8717.82 $-97.760$ 37.0570.103vK0.736.8117.07 $-104.00$ 33.9969.152IIMC1.546.2615.47 $-120.88$ 43.98106.84vK1.941.9414.86 $-125.93$ 47.66113.12IvK1.6218.888.27486.28225.3721.627MC1.5217.665.76299.07214.2088.894IIMKN2.697.8720.77 $-76.62$ 93.54132.47WHYC2.697.7720.69 $-77.26$ 93.54132.79IvK1.347.3513.01 $-141.35$ 43.04116.26MC1.147.0714.58 $-128.30$ 42.76109.22IMC1.659.3815.39 $-121.85$ 44.92110.23vK2.256.7715.68 $-119.39$ 52.31116.31IMC2.5317.374.83372.38312.85110.65vK2.7319.468.06316.06324.94153.32IvK1.5165.5667.02309.29171.96438.350MC1.4169.5275.94383.46165.9240.2697IIMC2.165.3418.91 $-92.515$ 60.900110.30

TABLE 5 Kinetic data on complexes<sup>a</sup>

<sup>*a*</sup>Unit of parameters: E /kJ mol<sup>-1</sup>, A /s<sup>-1</sup>,  $\Delta S^{\#}/kJ$  mol<sup>-1</sup>,  $\Delta H^{\#}/kJ$  mol<sup>-1</sup>,  $\Delta G^{\#}/kJ$  mol<sup>-1</sup>, *r*-correlation coefficient of the linear plot, *n*-order of reaction

following order: 2a < 2b < 2c < 2f < 2d < 2e. This result shows that 2e are more stable than others. It was found that the thermal stabilities and activation energies of the complexes for the first decomposition stage follow the order  $E_{2a} < E_{2c} < E_{2d} < E_{2f} < E_{2b} < E_{2e}$ . The highest thermal stability and activation energy for the first decomposition stage is displayed by the 2e complex.

#### **CONCLUSIONS**

In summary, we synthesized a series of novel cationic Pd(II) complexes with appropriate ligand precursors. A systematic study of the new complexes in Suzuki cross-coupling reactions afforded the following order of catalytic activities: 2f > 2c > 2d > 2e > 2a > 2b. Useful information has been collected about the influence of several structural factors, including the steric bulkiness around the Pd(II) center and the presence of electron-withdrawing groups on the aromatic ring of the imine fragment of the pydim ligands: when an electron withdrawing group was introduced into the the imine fragment, catalytic yield decreased. However, if an electron donating group was introduced into the imine fragment, catalytic yield was increased. A study on the thermal decomposition of the Pd(II) complexes was also carried out by using several kinetic methods. The decomposition kinetics was investigated by evaluating the dynamic thermogravimetric data obtained at a single heating rate. The activation energy E, the entropy change  $\Delta S^{\#}$ , enthalpy change  $\Delta H^{\#}$ , and Gibbs free energy change  $\Delta G^{\#}$ , were calculated by thermogravimetric analysis. It was found that the thermal stabilities and activation energies of complexes follow the order  $2a <\!\!2b < 2c <\!\!2f <\!\!2d <\!\!2e, E_{2a} < E_{2c} < E_{2d} < E_{2f} < E_{2b} < E_{2e},$ respectively.

#### REFERENCES

- Hofmeier, H., and Schubert, U.S. Recent developments in the supramolecular chemistry of terpyridine–metal complexes. *Chem. Soc. Rev.*, 2004, 33, 373–399.
- Desimoni, G., Faita G., and Quadrelli, P. Pyridine-2,6-bis(oxazolines), helpful ligands for asymmetric catalysts. *Chem. Rev.*, 2003, 103, 3119– 3154.
- Halcrow, M.A. The synthesis and coordination chemistry of 2,6bis(pyrazolyl)pyridines and related ligands — Versatile terpyridine analogues. *Coord. Chem. Rev.*, 2005, 249, 2880–2908.
- Gibson, V.C., Redshaw, C., and Solan, G.A. Bis(imino)pyridines: Surprisingly reactive ligands and a gateway to new families of catalysts. *Chem. Rev.*, 2007, 107, 1745–1776.
- Cuervo, D., Gamasa, M.P., and Gimeno, J. New chiral Ruthenium(II) catalysts containing 2,6-Bis(4'-(R)-phenyloxazolin-2'-yl)pyridine (Ph-pybox) ligands for highly enantioselective transfer hydrogenation of ketones. *Chemistry A European Journal*, 2004, 10, 425–432.
- Çetinkaya, B., Çetinkaya, E., Brookhart, M., and White, P.S. Ruthenium(II) complexes with 2,6-pyridyl-diimine ligands: synthesis, characterization and catalytic activity in epoxidation reactions. *J. Mol. Catal. A-Chem.*, **1999**, 141, 101–112.
- Tellmann, K.P., Gibson, V.C., White, A.J.P., and Williams, D.J. Selective dimerization/oligomerization of α-Olefins by Cobalt bis(imino)pyridine catalysts stabilized by Trifluoromethyl substituents: Group 9 metal cata-

lysts with productivities matching those of Iron Systems. *Organometallics*, **2005**, 24, 280–286.

- Miyaura, N., and Suzuki, A. Palladium-catalyzed cross-coupling reactions of organoboron compounds. *Chem. Rev.*, **1995**, 95, 2457–2483.
- Stanforth, S.P. Catalytic cross-coupling reactions in biaryl synthesis. *Tetrahedron*, 1998, 54, 263–303.
- Kotha, S., Lahiri, K., and Kashinath, D. New route to 4-Aminocyclopent-2-en-1-ols: Synthesis and enantioselective rearrangement of 4-Aminosubstituted cyclopentene oxides. *Tetrahedron*, 2002, 58, 9633–9640.
- Littke, A.F., and Fu, G.C. Palladium-catalyzed coupling reactions of aryl chlorides. *Angew. Chem.*, *Int. Ed.*, 2002, 41, 4176–4211.
- Liu, P., Zhang, W., and He, R. Preparation and catalytic properties of bis(imino)pyridine palladium(II) complexes as efficient catalysts for Suzuki cross-coupling reaction in water. *Appl. Organomet. Chem.*, **2009**, 23, 135– 139.
- Liu, P., Zhou, L., Xiaogang, L., and He, R. Bis(imino)pyridine palladium(II) complexes: Synthesis, structure and catalytic activity. *J. Organomet. Chem.*, 2009, 694, 2290–2294.
- Dogan, F., Kaya, I., and Bilici, A. Non-isothermal degradation kinetics of poly (2,2'-dihydroxybiphenyl). *Polym. Bull.*, 2009, 63, 2, 267–282.
- Kaya, I., Dogan, F., and Bilici, A. Schiff base-substituted polyphenol: synthesis, characterisation and non-isothermal degradation kinetics. *Polym. Int.*,2009, 58, 5, 570–578.
- Kaya, I., Baycan, F., and Dogan, F. Synthesis, characterization, conductivity, band gap and kinetic of thermal degradation of poly-4-[(2-mercaptophenyl) imino methyl] phenol. J. Appl. Polym. Sci., 2009, 112, 3, 1234– 1243.
- Doğan, F., Gülcemal, S., Yürekli, M., and Çetinkaya, B. Thermal analysis study of imidazolinium and some benzimidazolium salts by TG. *J. Therm. Anal. Cal.*, 2008, 91, 395–400.
- Kok, M.V. Temperature-controlled combustion and kinetics of different rank coal samples J. Therm. Anal. Cal., 2005, 79, 175–180.
- Doğan, F., Dayan, O., Yürekli, M., and Çetinkaya, B. Thermal study of ruthenium(II) complexes containing pyridine-2,6-diimines. *J. Therm. Anal. Cal.*, 2008, 91, 943–949.
- Sanchez, G., Garcia, J., Perez J., Garcia, G., Lopez G., and Villora, G. Thermal study of areneruthenium(II) derivatives. *Thermochim Acta*, 1997, 293, 153–161.
- Mentes, A., Fawcett, J., and Kemmitt, R.D.W. 2,6-Bis[1-(phenylimino)ethyl]pyridine. Acta Cryst., 2001, E57, o424–o425.
- Dayan, O., and Çetinkaya B. Mono- and binuclear ruthenium(II) complexes containing pyridine-2,6-diimine (Pydim) ligands: Synthesis, characterization and catalytic activity in the transfer hydrogenation of acetophenone. J. Mol. Catal. A-Chem., 2007, 271 134–141.
- Seckin, T., Köytepe, S., and Çetinkaya, E. Synthesis of new polyimides from Ru (II) complex of 2,6-bis[1-(p-dimethylaminophenylimino)ethyl]pyridine. J. Polym. Res., 2004, 11, 119–125.
- He-Kuan, L., Da-Gang, L., and Song, L. The effect of halide and the coordination geometry of chromium center in homogeneous catalyst system for ethylene trimerization. J. Mol. Catal. A-Chem., 2004, 221, 9–17.
- Madhusudanan, P.M., Krishnan, K., and Ninan, K.N. New equations for kinetic analysis of non-isothermal reactions. *Thermochim. Acta*, **1993**, 221, 13–21.
- MacCallum, J.R., and Tanner, J. The kinetics of thermogravimetry. *Eur. Polym. J.*, **1970**, 6, 1033–1039.
- Wanjun, T., Yuwen, L., Hen, Z., and Cunxin, W. New approximate formula for Arrhenius temperature integral. *Thermochim. Acta*, 2003, 408, 39–43.
- Van Krevelen, D.W., Van Heerden, C., and Huntjons, F.J. Kinetic study by thermogravimetry. *Fuel*, **1951**, 30, 253–258.
- 29. Doğan, F. Development of a computer program related to the methods of kinetic analysis of thermogravimetric data and its application to the kinetics of thermal decompositon and degradation of polymers. *Ph.D. Thesis*, Ege University, Izmir, Turkey, **2006**.