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New Pt(II) Complexes with Heterocyclic Ligands Derived from Benzimidazole: Synthesis, Characterization, DFT Calculations and Catalytic Activities

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Abstract

In this work, the synthesis, spectral characterization, DFT calculations, and catalytic activity of the new Pt(II) complexes with the ligand derived from benzimidazole derivatives have been described. The new heterocyclic ligands were obtained from the reaction of *o*-amino-ketones with hydrazine hydrate in high yieldandPt(II) complexes prepared from the coordination of the new ligands to Pt(II) cation. The new compounds have been characterized by spectral and microanalytical data. The DFT calculations at the B3LYP/6-311+G(d,p) level were also applied to gain further insight into the geometry of Pt(II) complexes. The catalytic activity of Pt(II) complexes in Biginellireaction was also examined as heterogeneous catalysts. The results showed that the 3,4-dihydropyrimidin-2(*1H*)-ones have been synthesized, in excellent yields, under solvent-free conditions, by reaction of tert-butyl acetoacetate, alcohol, arylaldehydes, and urea in the presence of Pt(II) complexes as an efficient and heterogeneous and catalyst.

Keywords: Pt(II) complex, DFT calculations, Benzimidazole, Biginelli reaction, Catalyst.

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Introduction

Platinum is one of the least reactive metals which have considerable corrosion resistance, even at high temperatures, and is therefore evaluated as a noble metal. Most applications of platinum are due to these properties and its high catalytic properties. Platinum is most commonly used in the manufacture of catalysts and jewelry. Other Pt uses include laboratory instruments, electrical connections and electrodes, medical and dental equipment, corrosion-resistant and corrosion-resistant devices, thermometers for electric furnaces, rocket covers, and jet engine fuels [1]. Also, Pt(II) complexes are promising entities for target-specific next-generation anticancer [2] and non-steroidal anti-inflammatory[3] drugs. They are also widely used as antibacterial [4], antiviral [5] antifungal [6], enzyme inhibitors [7], and chemical nucleases[8]. Moreover, Pt(II) complexes are employed as a catalyst in many reactions such as oxidation-reduction [9], polymerization [10], cycloaddition [11], and enantioselective alkylation [12] reactions. On the other hand, benzimidazole scaffold is one of the most important structures in heterocyclic aromatic organic compounds, because of its wide variety of potential functionalization and coordination modes. Current attention in benzimidazole moiety is stemming from their potential use as antimicrobial, antiviral, anti-inflammatory, and antitumor agents [13-16]. Recently, therapeutic applications of benzimidazoles have been reviewed [17].

Biginelli reaction is one of the most imperative types of multicomponent reaction and it offers a simple method to construct an N-heterocyclic moiety such as 3,4-dihydropyrimidin-2(*1H*)-one (DHPMs) was described by the Italian chemist Pietro Biginelli in 1893, involves a one-pot cyclocondensation of an aliphatic or arylaldehyde, a β-ketoester, and urea under strongly acidic conditions [18]. The increasing interest in the synthesis of DHPMs *via the* Biginelli reaction has demanded the development of new catalysts for the reason that traditional Biginelli reaction regularly suffers from insensitive reaction conditions, usage of harmful and non-volatile solvents, low yield, low selectivity, the requirement of high temperature, extended reaction time, etc [18-21]. Hence, a plethora of enhanced synthetic procedures based on the amendments of established Biginellicondensation have been developed during the past few years.

In light of the findings, two new Pt(II) complexes derived from benzimidazole ligands were synthesized and then characterized by analytical and spectroscopic methods. Moreover, Density functional theory (DFT) calculations were applied to provide the optimized geometries and structural parameters of the new complexes. The catalytic activity of the complexes was also evaluated for the synthesis of 3,4-dihydropyrimidin-2(1*H*)-one C5 ester derivatives *via*Biginelli/Transesterification multicomponent reactions as a new heterogeneous catalyst under thermal and solvent-free conditions.

Experimental

Equipment and Materials

Melting points were obtained on an Electrothermal type-9100 melting-point apparatus. The FT-IR spectra were recorded on potassium bromide pellets using a Tensor 27 spectrometer and only noteworthy absorptions were listed. The ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were acquired on a Bruker Avance DRX-300 spectrometer. Chemical shifts are reported in ppm downfield from TMS as an internal standard; the coupling constant is given as the *J* value in Hz. The percentage of Pt(II) was measured by using a Hitachi 2-2000 atomic absorption spectrophotometer. Elemental analysis was performed on a Thermo Finnigan Flash EA microanalyzer. The mass spectrum was recorded on a Varian Mat, CH-7 at 70 eV, and ESI mass spectrum was measured using a Waters Micromass ZQ spectrometer. All solvents were dried according to standard procedures. Compounds **2a,b**[22]**, 4a,b**[23] and **5a,b** [24] were obtained according to the published methods. Other reagents were commercially available.

Computational methods

The density functional theory (DFT) calculations were performed by using Gaussian 03 software package[25]. The B3LYP hybrid functional[26]and the 6-31+G(d,p) basis set were used, except for the Pt atom, where the LANL2DZ basis set[27]was employed. The geometry of the complex was fully optimized, which has no imaginary frequency in the frequency calculation. The sum of the electronic energies and the zero-point corrections (E+ZPE) were considered in the calculation of the electronic energies, which were obtained from the frequency calculations. The Polarizable-Continuum Model (PCM)[28]was employed to consider the solvent effects.

General procedure for the synthesis of ligands **6a,b**

To a solution of compounds **5a**,**b**(20 mmol) in EtOH (150 mL), hydrazine hydrate (1.6 g, 30 mmol) was added dropwise over 15 min with stirring. Then, the mixture was refluxed for 2 h and then poured into water. The precipitate was collected by filtration, washed with water, and air-dried to give crude **6a**,**b**. The product was purified by crystallization from ethanol to give yellow needles **6a,b.**

4-((4-Chlorophenyl)(hydrazono)methyl)-1-methyl-1H-benzo[d]imidazol-5-amine (**6a, L1**)

mp.: 209–211 $^{\circ}$C; Yield: 79%, IR (ν, cm^{-1}): 3349, 3283 (NH_2). ^{1}H NMR (DMSO-*d6*, δ, ppm): 4.17 (s, 3H, NCH_3), 6.39 (br s, 2H, NH_2), 6.83 (d, *J* = 8.9 Hz, 1H, Ar H), 7.38 (d, *J* = 8.9 Hz, 1H, Ar H), 7.81 (br s, 2H, NNH_2), 7.85 (d, *J* = 8.1 Hz, 2H, Ar H), 8.10 (s, 1H, Ar H), 8.59 (d, *J* = 8.1 Hz, 2H,

Ar H); ^{13}C NMR (DMSO-*d6*, δ, ppm): 38.1, 111.2, 116.4, 117.2, 123.0, 123.7, 127.6, 129.1, 130.7, 134.5, 136.1, 142.7, 158.3. MS (m/z) 299 (M^+). Anal. Calcd for $C_{15}H_{14}ClN_5$ (299.8) %: C, 60.10; H, 4.71; N, 23.36. Found (%): C, 59.89; H, 4.68; N, 23.49.

4-((4-Chlorophenyl)(hydrazono)methyl)-1-ethyl-1H-benzo[d]imidazol-5-amine (**6b, L2**)

mp.:195–197 °C; Yield: 74%, IR (ν, cm^{-1}): 3355, 3288 (NH_2).^{1}H NMR (DMSO-*d6*, δ, ppm): 1.38 (t, *J* = 7.5 Hz, 3H, CH_3), 4.34 (q, *J* = 7.5 Hz, 2H, NCH_2), 6.21 (br s, 2H, NH_2), 6.81 (d, *J* = 8.9 Hz, 1H, Ar H), 7.35 (d, *J* = 8.9 Hz, 1H, Ar H), 7.74 (br s, 2H, NNH_2), 7.89 (d, *J* = 8.1 Hz, 2H, Ar H), 8.09 (s, 1H, Ar H), 8.62 (d, *J* = 8.1 Hz, 2H, Ar H); ^{13}C NMR (DMSO-*d6*, δ, ppm): 17.2, 44.5, 111.3, 116.2, 116.9, 122.8, 123.8, 127.2, 129.3, 130.3, 134.7, 136.5, 142.7, 159.2. MS (m/z) 313(M^+). Anal. Calcd for $C_{16}H_{16}ClN_5$(313.8) %: C, 61.24; H, 5.14; N, 22.32. Found (%): C, 60.91; H, 5.11; N, 22.47.

*General procedure for the synthesis of the complexes **7a,b***

A solution of ligand **6a,b** (2 mmol) in acetone (10 mL) was mixed with a solution of K_2PtCl_4 (415 mg, 1 mmol) in water (10 mL). The reaction continued for another 4 h at rt. After concentration at reduced pressure, the precipitate was collected by filtration, washed with water, following with cold EtOH, and then air dried to give new complexes **7a,b.**More purification was obtained by crystallization from EtOH.

$[Pt(L1)_2]Cl_2$ (**7a**): m.p.> 300 ºC (decomp). IR (ν, cm^{-1}): ٣٤٧٥ (OH), ٣٣٦٥, ٣٢٤٣ (NH_2), 339, 345 (Cl-Pt).^{1}H NMR (DMSO-d_6 δ, ppm): 4.16 (s, 6H, NCH_3), 6.59 (br s, 4H, NH_2), 6.91 (d, *J* = 8.9 Hz, 2H, Ar H), 7.38 (d, *J* = 8.8 Hz, 2H, Ar H), 7.85 (d, *J* = 7.8 Hz, 4H, Ar H), 7.93 (br s, 4H, NNH_2), 8.04 (s, 2H, Ar H), 8.59 (d, *J* = 8.1 Hz, 4H, Ar H), ESI-MS (+) m/z (%): 793 $[Pt(L1)_2]^{2+}$. Anal. Calcd for $C_{30}H_{28}Cl_4N_{10}Pt$ (865.51) %: C, 41.63; H, 3.26; N, 16.18; Pt, 22.54. Found (%): C, 41.17; H, 3.20; N, 16.50; Pt, 22.89.

$[Pt(L2)_2]Cl_2$ (**7b**): mp> 300 ºC (decomp). IR (ν, cm^{-1}): 3479 (OH), 3381, 3263 (NH_2), 342, 346 (Cl-Pt).^{1}H NMR (DMSO-d_6 δ, ppm): 1.33 (t, *J* = 7.5 Hz, 6H, CH_3), 4.29 (q, *J* = 7.5 Hz, 4H, NCH_2), 6.62 (br s, 4H, NH_2), 6.93 (d, *J* = 8.9 Hz, 2H, Ar H), 7.41 (d, *J* = 8.8 Hz, 2H, Ar H), 7.86 (d, *J* = 7.8 Hz, 4H, Ar H), 7.91 (br s, 4H, NNH_2), 8.03 (s, 2H, Ar H), 8.62 (d, *J* = 8.1 Hz, 4H, Ar H), ESI-MS (+) m/z (%): 821 $[Pt(L1)_2]^{2+}$. Anal. Calcd for $C_{32}H_{32}Cl_4N_{10}Pt$ (893.56) %: C, 43.01; H, 3.61; N, 15.68; Pt, 21.83. Found (%): C, 42.78; H, 3.57; N, 16.04; Pt, 22.02.

Catalytic activity: Synthesis of 3,4-dihydropyrimidin-2(1H)-one C5 ester derivatives via Biginelli reaction via transesterification reaction

A mixture of tert-butyl acetoacetate **9** (1.0 mmol) and alcohol **11a-f** (1.5 mmol) was stirred for 30 min at 110 ^{o}C. The arylaldehyde **8a-e** (1.0 mmol), urea **10** (1.2 mmol), and catalytic amount (4.0 wt% of arylaldehyde) of Pt(II) complexes **7a,b** were added to the above mixture at rt under stirring. The prePtrsors were finely mixed and allowed to mechanical stirring for 2 hr at 80°C (oil bath) till the reaction was completed. After completion of the reaction, as indicated by TLC, it was cooled to room temperature and the reaction mixture was dissolved in cold EtOH (20 ml) and then the catalyst was separated by filtration. The catalyst was washed with cold EtOH three times and dried. The ethanolic solution containing crude product was evaporated until a precipitated pure product was formed. More purification was achieved by crystallization from EtOH and H_2O to afford 3,4-dihydropyrimidin-2(1*H*)-one C5 ester derivatives in high yield 83-95%. The structures of the products were confirmed from physical and spectroscopic data.

2-(Dimethylamino)ethyl 6-methyl-2-oxo-4-(p-tolyl)-1,2,3,4-tetrahydropyrimidine-5-carboxylate (**12a**)

mp.: 169-171°C [Lit mp. 168-170˚C][22].^{1}H-NMR (300MHz, $CDCl_3$): δ 2.20 (s, 6H), 2.31 (s, 3H), 2.32 (s, 3H), 2.42-2.44 (t, *J* = 5.8Hz, 2H), 4.12-4.13 (t, *J* = 5.8Hz, 2H), 5.37 (s, 1H), 5.61 (s, 1H), 7.11- 7.14 (d, *J* = 7.8Hz, 2H), 7.20-7.22 (d, *J* = 7.8Hz, 2H), 7.84 (s, 1H).

Prop-2-yn-1-yl 6-methyl-4-(4-nitrophenyl)-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (**12d**)

mp.: 182-184°C [Lit mp. 180-182˚C][22].^{1}H-NMR (300MHz, $CDCl_3$): δ 2.24 (s, 3H), 3.41-3.43 (t,1H), 4.66 (s, 2H), 5.31-5.33 (d, 1H), 7.47-7.49 (d, *J* = 8.8 Hz, 2H), 7.89 (s, 1H), 8.21-8.23 (d, *J* = 8.7 Hz, 2H), 9.51 (s,1H).

Isopentyl 4-(4-methoxyphenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (**12g**)

mp.: 168-170°C [Lit mp. 168-170˚C][22].^{1}H-NMR (300MHz, $CDCl_3$):δ 0.73-0.79 (d, 6H), 1.30-1.34 (m, 2H), 1.37-1.42 (m, 1H), 2.17 (s, 3H), 3.75 (s, 3H), 3.90-4.00 (m, 2H), 5.05-5.06 (d, 1H), 6.87-6.89 (d, *J* = 8.0 Hz, 2H), 7.10-7.12 (d, *J* = 8.0 Hz, 2H), 7.58 (s, 1H), 9.09 (s, 1H).

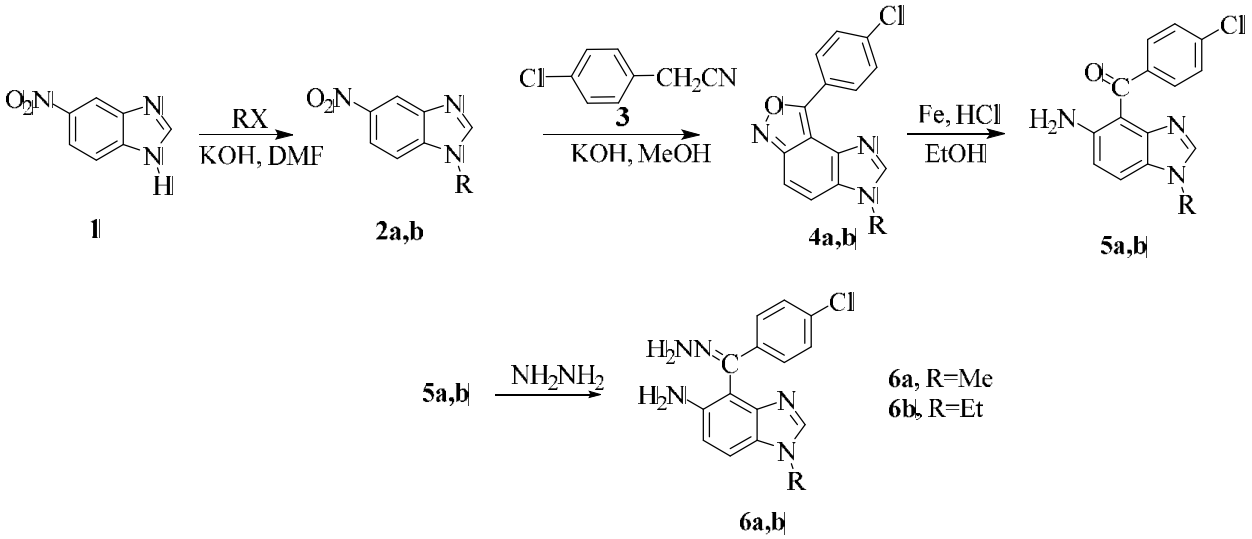
4-Methoxybenzyl 4-(4-methoxyphenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (**12j**)

mp.: 177-179°C [Lit mp. 178-180˚C][22].^{1}H-NMR (300MHz, $CDCl_3$): δ 2.19 (s, 3H), 3.70 (s, 3H), 3.69 (s, 3H), 4.96-497 (d, 2H), 5.11-5.13 (d, 1H), 6.78-6.82 (m, 4H), 7.11-7.17 (m, 4H), 7.62 (s, 1H), 9.06 (s, 1H).

Results and discussion

*Synthesis and structure of the new ligands **6a,b** and complexes **7a,b***

The alkylation of5-nitro-1*H*-benzimidazole (**1**) with methyl iodide and ethyl bromide in KOH and DMF led to the formation of1-alkyl-5-nitro-1*H*-benzimidazoles (**2a,b)** according to a literature method[22].The 6*H*-isoxazolo[4,3-*e*]benzimidazoles (**4a,b)** were obtained from the reaction of compounds **2a,b** with (4-chlorophenyl)acetonitrile**3** in basic MeOH solution[23].The compounds **4a,** were reduced to compounds **5a,b** by Fe/HCl in EtOH in high yields [24]. The new ligands **6a,b** were prepared by the reaction of the compounds **5a,** with hydrazine hydrate in EtOH as depicted in Scheme 1.



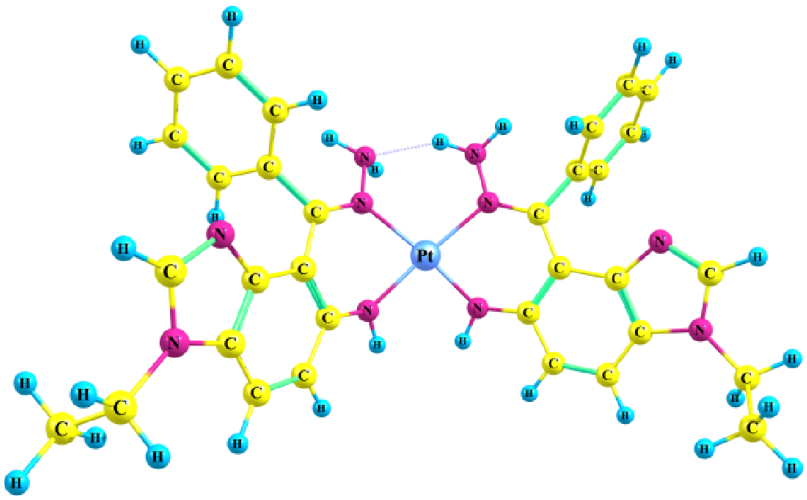
Scheme 1. Synthesis of the new ligands **6a,b.**

The structures of the new ligands **6a,b** were confirmed by the IR, mass, and NMR spectra as well as the elemental analyses. For example, the ^{1}H NMR spectrum of compound **6b** showed the ethyl group protons at δ 1.38 (t, *J* = 7.5 Hz, 3H, CH_3) and 4.34 (q, *J* = 7.5 Hz, 2H, NCH_2). Moreover, NH_2 group protons can be seen at δ 6.21 and 7.74 ppm. Four doublet signals 6.81 (d, *J* = 8.9 Hz, 1H, Ar H), 7.35 (d, *J* = 8.9 Hz, 1H, Ar H), 7.89 (d, *J* = 8.1 Hz, 2H, Ar H), 8.62 (d, *J* = 8.1 Hz, 2H, Ar H) and singlet signal (δ = 8.09 ppm) also appeared for seven protons of aromatic rings. Moreover, there are 14 different carbon atom signals in the ^{13}C NMR spectrum of compound **6b**. In the FT- IR spectrum of compound **6b**, a broad absorption band at 3355 and 3288 cm^{-1}can be attributed to NH_2 groups. Moreover, the results of mass spectroscopy and elemental analysis are in agreement with the structure of the ligand **6b**.

Finally, two new Pt(II)complexes **7a,b** were prepared by the coordination of ligands **6a,b** to Pt(II) cation in high yields. The stoichiometry of complexes **7a,b** (ML_2) was obtained by Job's method [29]. Nine aqueousmethanolic mixtures of ligands (0.6 mM) and Pt(II) (0.6 mM) were prepared in

the appropriate buffer at 25 °C. Sodium perchlorate was added to give a constant ionic strength of 0.1 M. The volumes of ligand solution used varied from 9 to 1 ml and those of Pt(II) solution from 1 to 9 ml; the total volume was always 10 ml. The absorption spectra of the complexes were achieved immediately after mixing the ligands and Pt(II) solutions.

Based on the stoichiometry of the complexes (ML_2), IR and NMR spectra, elemental analyses and mass spectral data, formulas $C_{30}H_{28}Cl_4N_{10}Pt$ and $C_{32}H_{32}Cl_4N_{10}Pt$were suggested for complexes **7a,b**. For example, in the FT- IR spectrum of complex **7a** a broad absorption band at a range of 3243-3475 cm^{-1} is assigned to OH and NH_2 groups and the absorption at 339 and 345 $cm^{-1}$are ascribed to the Pt-Cl band. In the ^1H NMR spectrum of complex **7a**, shifted NH_2 group protons are appeared at δ 6.59 ppm. Moreover, the results of mass spectroscopy (ESI-MS (+) m/z (%): 793 $[Pt(L1)_2]^{2+}$) and elemental analysis confirmed the proposed structure of the complex **7a**. Correspondingly, density functional theory (DFT) calculations were applied to obtain more detailed information about the geometry and structural parameters of the Pt(II) complexes **7a,b.**In the optimized geometry of complex **7b**, the **L** species acts as a bidentate ligand, and coordinates to the Pt^{2+} ion *via* the nitrogen atoms of the imine and amine groups. Based on experimental results and theoretical arguments, a square-planar geometry was proposed for the new Pt complexes **7a,b.** Also, the structure of the Pt(II) complexes **7a,b** could exist as two different isomers, *Cis* and *Trans*. In the *Cis* and *Trans* isomers of the complex, corresponding donating atoms of two **L**ligands lie in the same side and opposite sides to each other, respectively. For example, optimized geometries for the *Cis* and *Trans* isomers of complex **7b** have been shown in Figure 1.



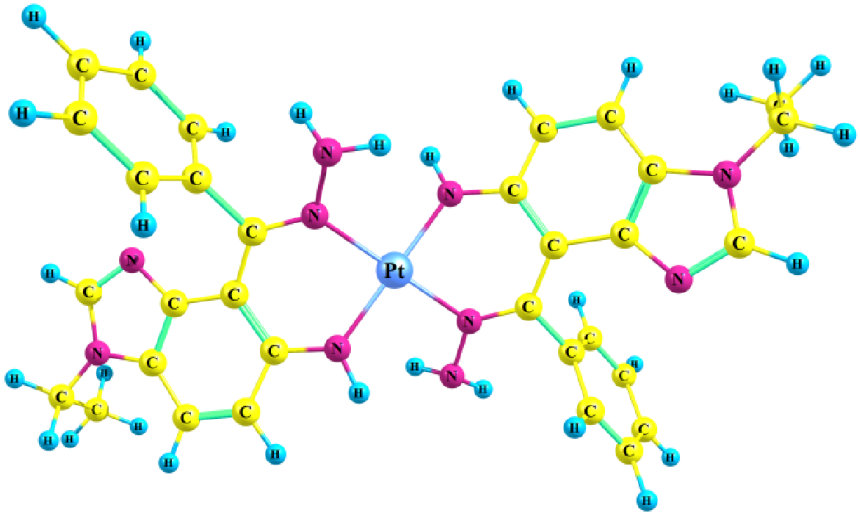


Figure 1. Optimized geometries for the *Cis* (up) and *Tans* (down) isomers of complex **7b**.

The calculated PCM energies exhibited that the *Trans* isomer of the Pt(II) complex **7b** is more stable than the *Cis* isomer by 229.47 kJ.mol^{-1}. This large energy difference between the *Cis* and *Trans*isomers confirmed that the solution of the new Pt(II) complexes involves only the *Trans* isomer. Also, the Gibbs free energy difference (ΔG) between the *Cis* and *Trans*isomers of the complex is the favorite of the Trans isomer. The calculated ΔG value in the methanol solution of the complex is 242.61 kJ.mol^{-1}. Based on this large ΔG value, the amount of the *Cis* isomer is predicted to be negligible in a solution of the Pt(II) complexes.

Some structural parameters of the complex**7b** were selected in Table 1. For comparison, reported structural parameters for the free **L** ligand **6b** were reported in Table 1. The calculated dihedral angles prove that the four coordinating atoms of two ligands as well as the Pt^{2+} metal ion are in the same plane. The calculated structural parameters are consistent with the reported data for similar compounds [30].

Table 1. Important structural parameters of the complex **7b** together with the free **L** ligand **6b**.

Species	L	[PtL_2]		L	[PtL_2]
Bond length (ppm)			**Angle (°)**		
C22-C1	145.3	145.1	C1-C6-N35	121.7	121.7
C1-C6	141.7	141.9	C6-N35-H36	132.6	132.9
C6-N35	136.6	137.6	Pt-N35-C6	-	124.9
N35-H36	102.6	101.3	C1-C2-C7	133.5	134.1
Pt -N35	-	218.9	C7-N8-N9	106.1	106.8
C22-C24	148.2	148.4	N8-N9-C12	121.3	121.4
C1-C2	146.8	147.3			
C7-N8	133.2	133.7			
N8-N9	136.9	136.4			

*Catalytic activity of Pt(II) complexes **7a,b***

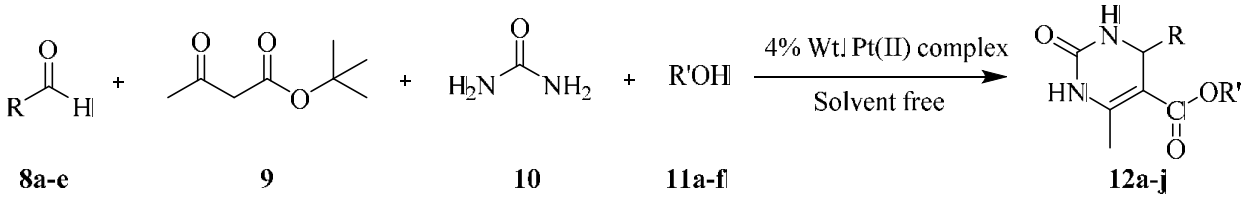
The carbonyl groups can be activated in starting material by complexes **7a,b,** and Lewis acid. To evaluate the activity of the Pt(II) complexes **7a,b** as a catalyst in the synthesis of 3,4-dihydropyrimidin-2(1*H*)-one C5 ester, the four-component reaction of 4-methoxybenzaldehyde (**8b**), tert-butyl-β-ketoester (**9**), urea (**10**) and propargyl alcohol (**11b**) (Scheme 2) was chosen as a model reaction to optimize the reaction conditions such as the molar ratio of the catalyst, temperature, and solvents. To select the appropriate solvent and temperature, the catalytic activity of Pt(II) complex **7a** was examined in toluene, ethanol, water, and solvent-free conditions. Based on the results, the highest yield of the desired product and maximum performance of the Pt(II) complex as catalyst was obtained once the reaction was carried out in solvent-free conditions at 110^{o}C.

To find optimum conditions of the amount of the catalyst for the preparation of DHPMs, the reaction of 4-methoxybenzaldehyde (**8b**), tert-butyl-β-ketoester (**9**), urea (**10**), and propargyl alcohol (**11b**) in the presence of Pt(II) complex **7a** in solvent-free conditions at 110^{o}C was carried out with varying amounts of the catalyst (1.0–6.0 Wt.% to aldehyde for catalyst concentration) and unchanging the reaction time to 2 hr. The results revealed that using 4.0 Wt.% to aldehyde for catalyst concentration is sufficient for achieving the best yield. The observed increase in the percentage conversion with increasing catalyst concentration can be due to the availability of a more active site on the catalyst surface during the reaction circumstance of four component Biginelli reaction followed by the transesterification process. However, a further increase in the catalyst concentration over 4.0 % might have increased the viscosity of the system which in turn reduces the interaction between the catalyst and reaction medium.

According to obtained optimal considered conditions, some3,4-dihydropyrimidin-2(1*H*)-one C5 ester were obtained and the results were reported in Table 2. An additional important quality of this procedure is the continued existence of a variety of functional groups, such as nitro, alkoxy, and

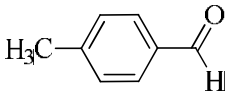
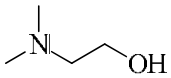
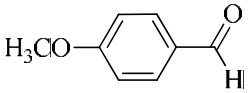
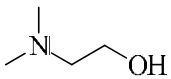
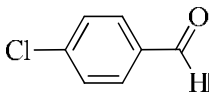
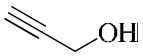
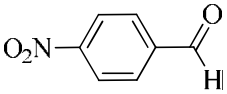
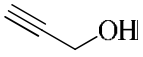
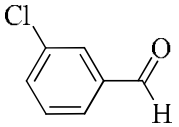
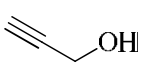
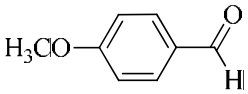
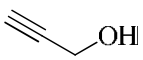
halides under reaction circumstances. In all these cases, the reactions were clean and the products were obtained with a simple work-up in excellent to outstanding yields.

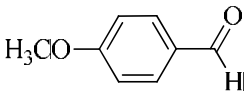
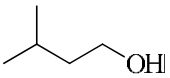
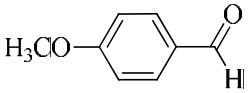
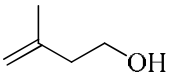
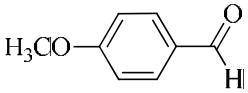
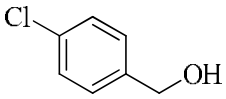
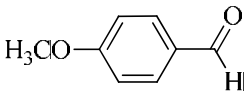
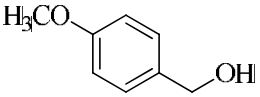
Pt(II) complex **7b** was also used as a catalyst in the synthesis of 3,4-dihydropyrimidin-2(1*H*)-one C5 ester derivative and the same results were obtained.



Scheme 2. Synthesis of various 3,4-dihydropyrimidin-2(1*H*)-one C5 estersusingPt(II) complex**7a** *via* Biginelli /Transesterification multicomponent reactions.

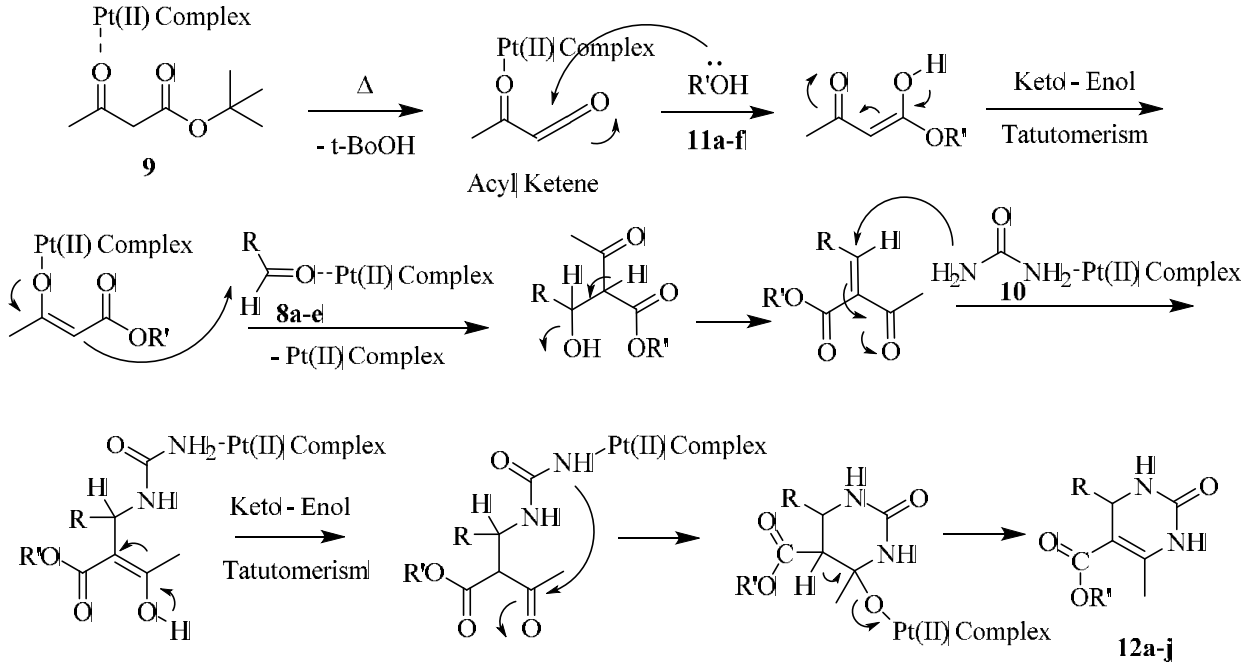
Table 2. Synthesis of some DHPMs in the presence of Pt(II) complex **7a** as catalyst under solvent-free condition[a]

Entry	Aldehyde/R	Alcohol/R'	Product	Yield/%[b]	M.p °C/Lit.[c][29]
1	 **8a**	 **11a**	**12a**	89	167-169 (168-170)
2	 **8b**	 **11a**	**12b**	92	158-160 (158-160)
3	 **8c**	 **11b**	**12c**	94	174-175 (174-176)
4	 **8d**	 **11b**	**12d**	88	179-181 (180-182)
5	 **8e**	 **11b**	**12e**	82	154-156 (156-158)
6	 **8b**	 **11b**	**12f**	95	195-196 (194-196)

7	 **8b**	 **11c**	**12g**	91	168-170 (168-170)
8	 **8b**	 **11d**	**12h**	94	153-155 (152-154)
9	 **8b**	 **11e**	**12i**	89	200-202 (200-202)
10	 **8b**	 **11f**	**12j**	86	177-179 (178-180)

[a]Reaction conditions: **8a-e**(1.0 mmol), **9**(1.0 mmol), **10**(1.2 mmol) and **11a-f**(1.5 mmol) at 110 [o]C, [b]Isolated yield, [c]The products were characterized by comparison of their spectroscopic and physical data with authentic samples synthesized by the procedure given in the references.

As depicted in Scheme 3, a reasonable reaction mechanism for the synthesis of 3,4-dihydropyrimidin-2(1*H*)-one C5 esters (DHPMs) using Pt(II) complexes**7a,b** was according to the exceeding enlightenment and the literature proceedings. The used Pt(II) complex **7a,b** contains Lewis acid in addition to basic surface sites. Initially, in transesterification transformation, *tert*-butyl-β-ketoester (**9**) coordination with Pt(II) complex enhances the electrophilicity of their carbonyl carbon underwent transacetoacetylation through acetylketene intermediate to form β-ketoester with alcohol. Aldehyde (**8a-e**) and β-ketoester with Pt(II) complex improve the electrophilicity of their carbonyl carbon. Then aldol-type condensation between aromatic aldehyde and β-ketoester forms the corresponding aldol-type product. In the next step, the electron-deficient sites present at the surface of the Pt(II) complex coordinate with the N-donor sites of urea (**10**) molecules and thus stabilize/ activate it for 1,4-addition reaction. This leads to the generation of adult products. Finally, cyclization of adult product by elimination of a water molecule results in the formation of DHPMs **12a-j**.



Scheme 3. Themultistep possible reaction mechanism for preparation of DHPMs in the presence of Pt(II) complexes as catalyst.

Comparing the efficiency of the present method with the previous methods [31-35] confirmed that the presented method has numerous advantages, which include operational simplicity, short reaction time and acceptable yields, no need for any chromatographic separation and a broad spectrum of substrate extent are the input features of this protocol.

Conclusion

New Pt(II) complexes were prepared by the reaction of new ligands derived from benzimidazole compounds with Pt cation. The new compounds were confirmed by spectral and analytical data. Furthermore, the optimized geometries and structural parameters of Pt(II) complexes were studied by the DFT calculations at the B3LYP/6-311+G(d,p) level. The catalytic activity of the Pt(II) complexes was also studied on the synthesis of 3,4-dihydropyrimidin-2(1*H*)-one C5 ester derivatives under thermal and solvent-free conditions. Based on the experimental results, this methodology reveals several advantages: up to 95% yield, operational simplicity, short reaction times, easy work-up procedure, and a greener approach compared with other methods reported in the literature. Also, an investigation of the catalytic activity of the complexes as heterogeneous catalysts in other organic reactions is in progress and will soon be published elsewhere.

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