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A case study of Pd ··· Pd intramolecular interaction in a benzothiazole based palladacycle; catalytic activity toward amide synthesis *via* an isocyanide insertion pathway[†]

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An acetate bridge benzothiazolepalladacycle containing a rare metallophilic intramolecular Pd···Pd interaction was synthesized and thoroughly characterized. The synthesized benzothiazolepalladacycle directly anchored on SBA-15 to form an efficient heterogeneous catalyst for amide synthesis *via* the migratory isocyanide insertion pathway.

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1. Introduction

The amide functional group has an important role in the synthesis of pharmacological compounds and materials.¹ The direct condensation of carboxylic acids and amines is the traditional route for amides synthesis which needs external acids or bases, wholly anhydrous conditions and high temperature. Indeed, it is not applicable for some of the sensitive substrates such as amino acids and natural products.² Due to the disadvantages and limitations, an alternative amide synthesis involves nucleophilic acyl substitutions through the pre- or in situ activation of the carboxylic acid partner (typically activation of the carboxylic group either as acyl chlorides or reactive anhydrides and esters or, alternatively, the use of coupling reagents).³ However, most of the methods suffer from limitations such as the use of toxic and expensive reagents, by-product generation and low atom economy. Additionally, due to unsuitable sterics and electronics, limitations in scope are still observed.³ Thus, the modern approaches of synthesizing amides focus on organoborons as a catalyst⁴ or mediator⁵ or transition metal-catalyzed reactions.^{6,7} Carbonylation of aryl halides with gaseous CO in the presence of amines is one of the TMC reactions for amide synthesis. Nevertheless, the use of CO and complicated ligands are the limitations of the reaction.⁶ The isocyanides (R-NC) and CO are isoelectronic and show similar reactivity.⁶ Recently, by the replacement of CO with R-NC, the transition metal-catalyzed reaction of aryl halides

and R-NC has been reported for amide synthesis *via* the migratory isocyanide insertion reaction (MIIr) in the absence of amine.⁸ The first study has been described by Jiang and co-workers using PdCl₂ and PPh₃ as an ancillary ligand.⁷ In 2014, the second study was reported by Yavari and co-workers using Cu₂O in the presence of phenanthroline-based ligands.⁹ The last study for isocyanide insertion into the Pd–C bond has been reported by Lei and co-workers.¹⁰ They used phenylboronic acids instead of aryl halides for amide synthesis *via* the MIIr strategy in the presence of a bimetallic Pd/Cu catalyst.

Cyclometalated Pd(II) complexes that contain a Pd–C bond are intramolecularly stabilized by at least one donor atom known as palladacycles.¹¹ They have emerged as a popular category of organometallic pre-catalyst for C–C and C–heteroatom coupling reactions.¹² A 2-Aryl benzothiazole ligand is a promising candidate for much broader application in palladacycle chemistry.¹³ Easy accessibility, thermal stability, participation in five-membered palladacycles¹⁴ and easily changing different substituents have motivated us to use this ligand in the amidation reaction *via* MIIr. Herein, for the first time, the migratory isocyanide insertion amidation was reported by a heterogeneous catalyst. The benzothiazolepalladacycle system was used as a common electron rich ligand.

2. Results and discussion

2.1. Synthesis and characterization of the catalyst

The preparation process of the benzothiazolepalladacycle (BTP) is illustrated in Scheme 1. First, the 4-hydroxyphenyl-benzothiazole (3) was synthesized by the reaction of 2-aminothiophenol (1) and 4-hydroxybenzaldehyde (2).¹⁵ The BTP was constructed by the



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Scheme 1 Synthesis of benzothiazolepalladacycle (BTP).

reaction of (3) and $Pd(OAc)_2$ in HOAc under an inert atmosphere under reflux conditions.¹⁴

The BTP was characterized by various techniques. The IR spectrum of BTP exhibits one broad absorption band for a carbonyl group of acetate at 1693 cm⁻¹, and two absorption bands for the C=N and C-S groups of a benzothiazole ring at 703 and 1604 cm⁻¹, respectively (ESI⁺). The ¹H-NMR spectrum of BTP shows a broad signal for the hydroxy group at 10.22 ppm. Moreover, the aromatic hydrogen atoms of BTP give rise to characteristic signals in the aromatic region. The best evidence for the formation of BTP is the appearance of a singlet up-field signal at 5.92 ppm related to the aromatic hydrogen near to Pd¹⁴ and a signal at 2.19 ppm for the acetate bridge¹⁶ (ESI[†]). The ¹³C-NMR of BTP shows two signals for the acetate bridge at 25.6 and 176 ppm plus characteristic signals of the aromatic region of the ligand. Moreover, the crystal structure determination (Fig. 1a) confirms the exact creation of the BTP complex containing dimeric Pd(II) centers coordinated to nitrogen of thiazole rings, carbons of the phenyl ring, and acetate bridges which grow in the P21 space group in an orthorhombic system. The geometrical parameters indicate lightly folded square-planar geometry around the palladium in which the angles (N1-Pd1-C9) and (N1-Pd1-O1) are 82.70° and 98.94°, respectively. Moreover, the benzothiazole ligands are transoid in the BTP dimeric backbone. The most desirable feature of BTP is a rare intramolecular palladium-palladium interaction. The small Pd1···Pd2 distance (2.862 Å) is 12.2% less than the sum of the van der Waals radius of two palladium atoms (3.26 Å) and longer than the sum of covalent radii (2.62 Å). The Hirshfeld diagram analysis around the Pd1···Pd2 axis demonstrates a high electrostatic potential, which indicates that Pd1 and Pd2 are involved in an interaction (Fig. 1b).

To scrutinize and clarify the existence and the nature of $Pd \cdots Pd$ (d8–d8) interaction, density functional theory (DFT) calculations, quantum theory of atoms in molecules (QTAIM) analysis, the natural bond orbital (NBO) method, and non-covalent interaction reduced density gradient (NCI-RDG) analysis were performed. Noticeably, the selected data regarding $Pd \cdots Pd$ interaction were cut out directly from the crystallographic



Fig. 1 (a) The asymmetric units of BTP and the thermal ellipsoids at the 40% probability level (all of hydrogen atoms and MeOH as crystallization solvent are omitted for clarity); (b) electrostatic potential of the Pd1 \cdots Pd2 axis analyzed by the Hirshfeld diagram. High electron density is depicted as red and low electron density as blue.

Information File (CIF). The geometrical parameters of the optimized structure and experimental X-ray structure revealed a successful optimization (ESI⁺). The NBO analysis was performed to evaluate the Pd...Pd interaction. This analysis reveals that BD (bonding), CR (Atomic Core State), LP (Lone Pair) and LP* (Lone Pair star) orbitals of a Pd1 atom act as a donor, while LP*, RY* (Rydberg State), and BD* (Anti Bonding) orbitals of a Pd2 atom act as an acceptor. From the other side, LP, LP*, and BD* orbitals of the Pd2 atom act as a donor, while LP*, RY*, and BD* orbitals of the Pd1 atom act as an acceptor. The existence of metallophilic interaction between two palladium atoms with the donor-acceptor nature was graphically shown by molecular orbitals. The HOMO and LUMO orbitals and the gap between them have been calculated (Fig. 2). As a result of high electron density between the Pd1…Pd2 axis in the HOMO of BTP, the Pd atoms and the ligands have more contributions in the HOMO and LUMO, respectively (Scheme 2).

The QTAIM is a potent and applicable tool to analyse chemical bonds and interactions in various aspects.¹⁷ As can be seen in the molecular graph of the BTP (Fig. 3) and contour map of the electron density's Laplacian (ESI[†]), the bond critical point (BCP) between two palladium atoms discloses an interaction between two palladium atoms. To elucidate this interaction, some applications of the QTAIM were used. Based on Bader's criteria,¹⁸ the electron density of BCP (ρ_{BCP}) for a closed-shell interaction is less than 0.10 a.u. Consequently, the Pd···Pd interaction in BTP with $\rho_{BCP} = 0.0171$ a.u. is a closed-shell interaction. Likewise, based on the positive value



of electron density laplacian ($\nabla^2 \rho_{BCP}$), this interaction categorises as a closed-shell one. According to kraka's criteria,¹⁹ the positive value of local energy density at BCP (H(BCP)) proves the closed-shell nature for an interaction observable for (H(BCP)) of Pd···Pd interaction. Similarly, by Espinosa's criteria,²⁰ the Pd···Pd interaction displays a closed-shell interaction with (|V(BCP)|/G(BCP)) < 1 and for BTP = 0.965. All results of theoretical studies corroborated a closed shell or a non-covalent interaction. Moreover, mapping the real-space was obtained by the (NCI-RDG). This method is based on the electron density and its gradient $(sign(\lambda 2)\rho)$.^{21,22} The Pd · · Pd interaction was evaluated by NCI-RDG and the results of $s(\rho)$ versus sign $(\lambda 2)\rho$ and $s(\rho)$ isosurface have been shown in Fig. 3B and C. According to the plots, the negative value of $sign(\lambda 2)\rho$ and the green colour isosurface between two palladium atoms demonstrate a van der Waals nature of this interaction. Based on the experimental and theoretical findings the Pd···Pd interaction in the BTP case study is an intramolecular d^8-d^8 metallophilic interaction. In addition, the bond order of the Pd…Pd interaction was calculated by two NBO criteria; Wiberg bond indices and NAO (natural atomic orbital) bond order. The calculated bond orders based

Scheme 2 Synthesis of BTP@SBA



Fig. 3 (a) The molecular graph for BTP determined by the B3LYP/ LANL2DZ computational level. The green dots stand for the bond critical points (BCPs), the red dots stand for the ring critical points (RCPs), and the blue ones stand for cage critical points (CCPs). Red, white, blue, gray and yellow atoms represent O, H, N, C and S elements, respectively. (b) The plots of RDG, $s(\rho)$, *versus* sign($\lambda 2$) ρ , and finally (c) coloured $s(\rho)$ -isosurface in B3LYP/LANL2DZ computational methods.

Wiberg bond indices and NAO are 0.0912 and 0.1814, respectively (ESI[†]).

After BTP characterization, the BTP was directly anchored to SBA-15 to form a heterogeneous catalyst (Scheme 3). For the synthesis of the heterogeneous catalyst, the SBA-15 was reacted with thionyl chloride to afford the corresponding chlorinated SBA-15 (SBA-Cl).²³ Finally, the benzothiazolepalladacycle bonded



to SBA-15 (BTP@SBA) was formed by the addition of the dried solution of BTP to dispersed SBA-Cl.

The BTP@SBA catalyst was characterized by thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FT-IR), flame atomic absorption (FAAs), energy-dispersive Xray spectroscopy (EDX), transmission electron microscopy (TEM), scanning electron microscopy (SEM), small angle X-ray scattering (S-XRD) and nitrogen sorption analysis. The FT-IR spectrum of the catalyst exposed a broad characteristic between 1000 and 1200 cm⁻¹ for Si–O–Si stretching bonds of the SBA structure. Additionally, a peak at 1667 cm⁻¹ is related to the carbonyl group of acetate bridges of BTP (ESI†). The surface composition was determined by EDX. The elements of Si, Pd, O, C, N, and S in the EDX spectrum are related to the BTP modified on SBA-15 (Fig. 4).

TGA was further used to study the heating resistance of the catalyst (Fig. 5). A TGA plot of the catalyst shows a weight loss at ~ 100 °C, which was assigned to adsorbed water. The 6.95% weight loss at above ~ 300 °C (and continuing up to ~ 530 °C) is related to the decomposition of covalently bonded organic



Fig. 4 The EDX elemental analysis of BTP@SBA.



groups from the catalyst. This demonstrates that the catalyst has suitable thermal stability until ~300 °C. The palladium content of the catalyst was calculated (0.49 mmol g⁻¹) by FAAs.

The small-angle ($0 < \theta < 10^{\circ}$) XRD pattern of SBA-15 and BTP@SBA indicates the two-dimensional hexagonal ordered symmetry with a typical pattern of the (100) plane of mesopores $(2\theta = 1.47^{\circ})$ (Fig. 6a). This proves that modification of SBA-15 with BTP does not affect the crystallinity of SBA-15.²⁴ The SEM images reveal that the BTP@SBA particles have a nearly regular hexagonal shape²⁵ with the particle size in the range of 400 nm $(\pm 50 \text{nm})^{26}$ (Fig. 6b). N₂(g) adsorption-desorption of the catalyst shows typical IV type curves in which the surface area and pore volume of the catalyst are 329.31 m² g⁻¹ and 0.5629 cm³ g⁻¹, respectively (ESI[†]). The surface area and pore volume of BTP@SBA are smaller than the fresh SBA-15 (726 $m^2 g^{-1}$ and 0.9842 cm³ g⁻¹). This indicates the BTP anchored mostly inside the channel of SBA-15. Furthermore, the value of Barrett-Joyder-Halenda (BjH) (ESI[†]) shows an average pore diameter of 3.58 nm in excellent agreement with the TEM result (ESI⁺). Likewise, the BJH distribution curve depicts a narrow pore size distribution (less than 10 nm).

The TEM image of BTP@SBA displays highly ordered mesoporous channels with a complete 2D (*P6mm*) hexagonal



Fig. 6 (a) The low angle P-XRD of BTP@SBA; (b) the SEM image of BTP@SBA.

arrangement of mesoporous. This shows the absence of Pd nanoparticles on the surface of silica or inside the channels (Fig. 7). Notably, the channels were largely preserved during modification of BTP on SBA-15 and even under reflux of SOCl₂ during catalyst preparation.²⁷



Fig. 7 The TEM of BTP@SBA along the pore axis of BTP@SBA.

2.2. Catalytic activity of BTP@SBA

After preparation and characterization of BTP@SBA, its catalyst performance and selectivity were appraised in MIIr of aryl halides and isocyanides. First, the various solvents, temperatures, bases, amount of catalyst, and reaction times were tested to obtain the best reaction conditions (Table 1). An initial assessment of the catalytic activity of BTP@SBA (0.5 mol% with respect to Pd content) for an amidation reaction via MIIr was tested for the reaction of Ph-I (4a) and *tert*-butyl isocyanide (5b) as a model reaction. The reaction at 100 $^{\circ}$ C in DMSO and in the presence of K₂CO₃ gave 67% isolated yield of the corresponding amides (6a) (Table 1, entry 1). Then, some inorganic and organic bases such as K₂CO₃, Cs₂CO₃, Et₃N, NaOH and CsF were tested in the model reaction in DMSO at 100 °C (Table 1, entries 1-5). The results show that the Cs₂CO₃ was the superlative base (entry 2). Afterward, the effect of Pd content was investigated using Cs₂CO₃ as an ideal base. When the amount of Pd increased from 0.5 to 1 and 1.5 mol%, the isolated yield of the corresponding amide was not affected impressively (entries 2, 6 and 7). 0.3 mol% of the catalyst resulted in the amidation in lower yield (entry 8). When the reaction was carried out without catalyst, the isolated yield of the corresponding amide was trace (entry 9). Therefore, 0.5 mol% of Pd content was sufficient to push the reaction forward. To monitor the effect of temperature, the reaction was carried out at room temperature, 60, 80, and 120 °C to result in the product in trace, 31, 54 and 68% isolated yield, respectively (entries 10-13). Finally, DMSO, CHCl₃, DMF, toluene, H₂O and DMSO/H₂O (1:1) were checked as different solvents in the MIIr reaction (entries 14-18). As shown, the reaction worked most efficiently in DMSO/H2O (1:1) (entry 18). The optimum conditions were obtained with

Table 1 Screening the reaction conditions

Р	$\mathbf{h}-\mathbf{I} + (\mathbf{M}\mathbf{e})_3 \mathbf{C}-\mathbf{I}$	► Ph-CO	Ph-CO-NHC(Me) ₃			
4a 5a				6a		
Entry	Catalyst (mol%)	Base	Solvent	$T(^{\circ}C)$	Yield ^a (%)	
1	0.5	K ₂ CO ₃	DMSO	100	65	
2	0.5	Cs_2CO_3	DMSO	100	68	
3	0.5	Et ₃ N	DMSO	100	Trace	
4	0.5	NaOH	DMSO	100	43	
5	0.5	CsF	DMSO	100	66	
6	1	Cs_2CO_3	DMSO	100	69	
7	1.5	Cs_2CO_3	DMSO	100	69	
8	0.3	Cs_2CO_3	DMSO	100	48	
9	_	Cs_2CO_3	DMSO	100	Trace	
10	0.5	Cs_2CO_3	DMSO	80	54	
11	0.5	Cs_2CO_3	DMSO	60	31	
12	0.5	Cs_2CO_3	DMSO	120	68	
13	0.5	Cs_2CO_3	DMSO	r.t	Trace	
14	0.5	Cs_2CO_3	CHCl ₃	reflux	Trace	
15	0.5	Cs_2CO_3	DMF	100	63	
16	0.5	Cs_2CO_3	Toluene	100	49	
17	0.5	Cs_2CO_3	H_2O	reflux	18	
18	0.5	Cs_2CO_3	DMSO/H ₂ O (1:1)	100	73	

Iodobenzene (1 mmol), t-BuNC (1.2 mmol), base (1 mmol) for 24 h. a Isolated yields.

 Cs_2CO_3 as a base and DMSO/H₂O as a solvent using 0.5 mol% of BTP(a)SBA at 100 °C for 24 h.

To explore the scope of the reaction, diverse Ar-X 4 and isocyanides 5 were screened in the reaction (Scheme 3). All aryl iodides gave reasonable isolated yields without significant by-products. Notably, superior activity for the amidation reaction was obtained with cyclohexylisocyanide (6b). The reaction with Ar-Br produced the desired amides in moderate yields. The Ar-Cl with electron donating and electron withdrawing groups were tested and the yields of products were trace (Scheme 3). The (Het)Ar-Cl afforded the desired amides in good yields (6m, 6n). To the best of our knowledge, there are no examples of employing any heterogeneous catalysts and palladacycle complexes for amide synthesis by MIIr.

The reusability and stability are hallmarks of heterogeneous catalysts. To specify BTP@SBA is operating in a heterogeneous or homogeneous pathway, a hot filtration test was performed for MIIr of Ph-I and t-Bu-NC.²⁸ In this way, the reaction was stopped after the midpoint of reaction (12 h). Subsequently, the hot filtrate was rapidly transferred to another vessel containing Cs₂CO₃ and DMSO/H₂O at 100 °C. By heating the catalyst-free flask for 12 h, no significant progress was observed. Moreover, using FAAs, the same reaction solution at the midpoint of reaction completion indicated that no significant quantities of palladium were lost to the reaction liquors during the process.²⁹ The recyclability of the catalyst was also studied in the MIIr reaction of Ph-I and t-Bu-NC. After the accomplishment of each run of the reaction, the catalyst was extracted by centrifugation, followed by washing with an excess amount of MeOH and acetone. The catalyst could be reused at least five times successfully without significant loss in activity (yields: 73%, 73%, 71%, 69%, and 68%). Furthermore, the small angle XRD analysis of the recycled BTP@SBA demonstrated the homogeneity of the pores (ESI[†]). Moreover, the low angle sharp peak was retained after five runs (Fig. 8a). The SEM image of reused BTP@SBA proved the approximately hexagonal structure (Fig. 8b). Besides, the TEM analysis after five catalytic cycles showed no conclusive evidence of colloidal Pd species $(Pd^{0}-L)^{30}$ (Fig. 8c). The mercury poisoning test for MIIr does not show a remarkable discrepancy in isolated yield for 3a synthesis. The results support that the BTP@SBA catalyzes the MIIr reaction by a quasi-heterogeneous nature that takes place mainly via Pd⁺²/Pd⁺⁴ catalytic cycles. The proposed mechanism can be found with more details in the ESI.†

3. Experimental

3.1. Materials

All chemicals were purchased from Merck or Aldrich and were used without additional distillation. FT-IR spectra were taken using a Bomem FT-IR MB spectrometer. The NMR spectra were recorded on a BRUKER DRX-300 AVANCE spectrometer. Powder X-ray Diffraction data were collected on a STOE STADI P with a scintillation detector, secondary monochromator and Cu-Ka1 radiation ($\lambda = 1.5406$ Å). EDS characterization of



Fig. 8 (a) The powder XRD pattern; (b) the SEM image; and (c) the TEM of reused BTP@SBA after 5 catalytic cycles.

BTP@SBA was performed using an electron microscopy Philips XL-30 ESEM. Transmission Electron Microscopy characterization of BTP@SBA was performed using a Philips CM-30 transmission microscope with an accelerating voltage of 150 kV. The concentration of Pd was estimated using a Shimadzu AA-680 flame atomic absorption spectrophotometer. The sorption analysis was recorded by micromeritics Auto-chem II 2920. Furthermore, TGA was accomplished by PerkinElmer TGA/DSC. Lastly, the CHNS content was estimated by a PerkinElmer 2400 series.

The X-ray diffraction measurements were performed with a STOE IPDS-II diffractometer with graphite-monochromated MoKa radiation. Cell constants and an orientation matrix for data collection were obtained by least-squares refinement of diffraction data from 6743 and 3408 unique reflections for BTP. Data were collected at a temperature of 298(2) K to a maximum 2q value of 51.988 and in a series of w scans in 18 oscillations and integrated using the Stoe X-AREA software

package. The data were corrected for Lorentz and Polarizing effects. The structures were solved by direct methods and refined on F2 by a full-matrix least-squares procedure. All hydrogen atoms were added at ideal positions and constrained to ride on their parent atoms, with $U_{\rm iso}({\rm H}) = 1.2 U_{\rm eq}$. All refinements were performed by using the X-STEP32 crystallographic software package. Complete crystallographic data for BTP have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1968870.†

3.2. Synthesis of 4-hydroxy 2-phenyl benzothiazole (3)

The 2-aminothiophenol (1 mmol) and 4-hydroxybenzaldehyde (1 mmol) were stirred in MeOH at room temperature to afford yellow imine sediment. Subsequently, NH_2SO_3H (10 mol%) was added to the reaction mixture. After 4 h, light yellow sediment was achieved and recrystallized in MeOH/H₂O to afford a pure product.

3.3. Synthesis of 4-hydroxy 2-phenyl benzothiazole palladacycle (BTP)

The dimeric acetate palladacycle (**BTP**) was obtained by the reaction of (3) (1 mmol) and $Pd(OAc)_2$ (1 mmol) in HOAc under reflux conditions and an inert atmosphere for 2 h. Afterward, an excess amount of *N*-hexane was added to the reaction mixture and the sediment gained by simple filtration as a greyish-green colour.

3.4. Synthesis of chlorinated SBA-15

Fresh SBA-15 was kept overnight under 120 $^{\circ}$ C to evaporate adsorbed water. The SBA-Cl was obtained by chlorination of dried SBA-15 nanoparticles. SBA-15 (3 g) was refluxed in 60 mL SOCl₂ in a round bottomed flask fortified with a drying tube, condenser and inert atmosphere for 24 h. The excess amount of thionyl chloride was distilled off and the resulting solid product was flame-dried as a light-greyish colour and stored in a sealed vessel under N₂(g).

3.5. Synthesis of BTP directly bonded to SBA-15 (BTP@SBA)

The BTP (0.5 mmol, 0.39 g) was dissolved in 40 mL dried DMF. The soluble of BTP was added dropwise to the round bottom flask containing dried chlorinated SBA-15 under $N_2(g)$. The reaction was accompanied by emission of gaseous HCl. The reaction was stirred for 24 h at room temperature. Then, 60 ml of MeOH was added to the reaction. Afterward, the BTP@SBA was separated by centrifugation and washed several times with MeOH and H_2O in order to neutralize the pH.

3.6. General procedure for the migratory isocyanide insertion reaction

A mixture of arylhalides (1 mmol), isocyanides (1.2 mmol) and Cs_2CO_3 (1 mmol) in the presence of 0.5 mol% of BTP@SBA in DMSO/H₂O (2 mL, 1:1) was stirred at 100 °C for 24 h. After completion of the reaction (TLC), the reaction mixture was cooled to room temperature. Then, MeOH (5 mL) was added to the reaction mixture and the solid BTP@SBA was separated by filtration. The filtrate was evaporated under vacuum and the

product was purified by Column chromatography (EtOAc/*n*-Hexane (3/7)).

4. Conclusions

In this work, a benzothiazolepalladacycle containing metallophilic $Pd \cdots Pd$ intramolecular interactions was synthesized and characterized by using experimental and computational methods. Furthermore, the heterogenized system of the organometallic complex was found to be an easy-synthesis and efficient catalyst for amidation reaction *via* the migratory isocyanide insertion pathway. The availability of the catalyst, recyclability and use of small amounts of palladium precursor in a vital reaction model in the isocyanide insertion area are important features of this study.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

- A. Ojeda-Porras and D. Gamba-Sánchez, *J. Org. Chem.*, 2016, 81, 11548.
- 2 R. M. de Figueiredo, J.-S. Suppo and J.-M. Campagne, *Chem. Rev.*, 2016, **116**, 12029.
- 3 E. Massolo, M. Pirola and M. Benaglia, *Eur. J. Org. Chem.*, 2020, 4641.
- 4 L. Gu, J. Lim, J. L. Cheong and S. S. Lee, *Chem. Commun.*, 2014, **50**, 7017.
- 5 V. Karaluka, R. M. Lanigan, P. M. Murray, M. Badland and T. D. Sheppard, *Org. Biomol. Chem.*, 2015, **13**, 10888.
- 6 K. Dahl, M. Schou, N. Amini and C. Halldin, *Eur. J. Org. Chem.*, 2013, 1228.
- 7 H. Jiang, B. Liu, Y. Li, A. Wang and H. Huang, *Org. Lett.*, 2011, **13**, 1028.
- 8 M. Shiri, N. Farajinia-Lehi, P. Salehi and Z. Tanbakouchian, *Synthesis*, 2020, 3162.
- 9 I. Yavari, M. Ghazanfarpour-Darjani and M. J. Bayat, *Tetrahedron Lett.*, 2014, 55, 4981.
- F. Lu, Z. Chen, Z. Li, X. Wang, X. Peng, C. Li, L. Fang, D. Liu, M. Gao and A. Lei, *Org. Lett.*, 2017, **19**, 3954.
- 11 J. Dupont, C. S. Consorti and J. Spencer, *Chem. Rev.*, 2005, 105, 2527.
- 12 X. Gai, R. Grigg, M. Imran Ramzan, V. Sridharan, S. Collard and J. E. Muir, *Chem. Commun.*, 2000, 2053.
- 13 A. Bruneau, M. Roche, M. Alami and S. Messaoudi, *ACS Catal.*, 2015, 5, 1386.

- 14 M. R. Churchill, H. J. Wasserman and G. J. Young, *Inorg. Chem.*, 1980, **19**, 762.
- 15 A. Rostami and A. Yari, J. Iran. Chem. Soc., 2012, 9, 489.
- 16 F. d'Orlyé and A. Jutand, Tetrahedron, 2005, 61, 9670.
- 17 R. F. W. Bader, *Atoms in Molecules- A Quantum Theory*, Clarendon, Oxford, 1990.
- 18 R. F. Bader and H. Essén, J. Chem. Phys., 1984, 80, 1943.
- 19 D. Cremer and E. Kraka, Croat. Chem. Acta, 1984, 57, 1259.
- 20 E. Espinosa, I. Alkorta, J. Elguero and E. Molins, *J. Chem. Phys.*, 2002, **117**, 5529.
- 21 E. R. Johnson, S. Keinan, P. Mori-Sánchez, J. Contreras-García,
 A. J. Cohen and W. Yang, J. Am. Chem. Soc., 2010, 132, 6498.
- 22 J. Contreras-García, E. R. Johnson, S. Keinan, R. Chaudret, J.-P. Piquemal, D. N. Beratan and W. Yang, *J. Chem. Theory Comput.*, 2011, 7, 625.

- 23 A. Feiz and A. Bazgir, Catal. Commun., 2016, 73, 88.
- 24 A. Sayari, B.-H. Han and Y. Yang, J. Am. Chem. Soc., 2004, 126, 14348.
- 25 A. J. Crisci, M. H. Tucker, M.-Y. Lee, S. G. Jang, J. A. Dumesic and S. L. Scott, ACS Catal., 2011, 1, 719.
- 26 H. Tüysüz, C. W. Lehmann, H. Bongard, B. Tesche,
 R. Schmidt and F. Schüth, *J. Am. Chem. Soc.*, 2008, 130, 11510.
- 27 B. Karimi and H. Behzadnia, Synlett, 2010, 2019.
- 28 B. Karimi, S. Abedi, J. H. Clark and V. Budarin, Angew. Chem., Int. Ed., 2006, 45, 4776.
- 29 A. Feiz, M. Loni, S. Naderi and A. Bazgir, *Appl. Organomet. Chem.*, 2018, **32**, e4608.
- 30 C. M. Crudden, M. Sateesh and R. Lewis, J. Am. Chem. Soc., 2005, 127, 10045.