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Monodentate palladium(0)-[60]fullerene complexes of diphosphine ligands as efficient and sustainable nanocatalysts for Mizoroki-Heck coupling reaction of aryl chlorides

Seyyed Javad Sabounchei^{a*}, Marjan Hosseinzadeh^a, Morteza Zarepour-jevinani^b

and Bahram Ghanbari^b

^a Faculty of Chemistry, Bu-Ali Sina University, Hamedan,65174, Iran
^b Department of Chemistry, Sharif University of Technology, PO Box 11155-3516, Tehran, Iran

Abstract

of fullerene[60] Two mononuclear coordination complexes with $Pd(dba)_2$ (dba= dibenzylideneacetone), $[(\eta^2 - C_{60})Pd(Ph_2P(CH_2)_2PPh_2 = C(H)C(O)R)_2]$ (R= $C_{10}H_7$ (1), $C_6H_4Cl(2)$), have been prepared through a simple procedure to explore new directions in palladium catalysis nanocarbon chemistry. The palladium(0)-[60]fullerene complexes incorporating and unsymmetrical phosphorus ylides have been characterized by ¹H, ¹³C and ³¹P NMR spectroscopic methods and other conventional techniques such as IR, TGA, SEM, ICP-OES, EDX and TEM analysis. Attributed to the enhanced dispersity and uniform size of Pd nanoparticles with phosphine-functionalized fullerenes, the prepared catalysts exhibited comparable catalytic activity to those reported for Mizoroki-Heck coupling reaction of aryl chlorides. Because of their abundance and low cost, aryl chlorides are the most desirable substrates from an industrial point of view in Csp²-Csp² coupling reactions. Furthermore, overall bonding modes in the palladafullerenes of bifunctional diphosphine-based ligands were investigated by spectroscopic analysis and theoretical calculations. DFT studies of geometryoptimized monodentate and bidentate structures for 1 were calculated at the B3LYP/LANL2MB level of theory to understand the origin of the observed coordination modes.

^{*} Corresponding author. E-mail address: jsabounchei@yahoo.co.uk (S.J. Sabounchei).

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Keywords: Fullerene; Phosphorus ylide; Palladium nanocatalyst; Heterogeneous; Heck reaction.

Introduction

The discovery of fullerenes in 1985 by Kroto, Curl and Smalley¹ opened up new vistas in nanoscience and marked the beginning of a new field of chemical research. Transition metal-fullerene systems are currently challenging topics of interest for their modern chemistry, physicochemical properties, and outstanding biological activities.^{2,3} In addition, the synthesis of such fullerene-containing complexes and related carbon nanostructures offers the potential to exploit the chemical reactivity, redox and electron acceptor characteristics, magnetic and optical activity and novel structural features.^{4,5} Although there are many precedents for the preparation of metallofullerenes,⁶⁻⁸ only few studies on the palladium-fullerene complexes containing phosphorus ligands have been reported so far. As the versatile functionalized diphosphines such as α -keto stabilized phosphorus ylides can be coordinated to C₆₀ and palladium core through the free PPh₂ group and/or formally negatively charged carbanion,⁹ they are interesting for subsequent coordination chemistry studies (Scheme 1).



Scheme 1. Mono- and bidentate palladium(0)-[60]fullerenes containing dppe (1,2bis(diphenylphosphino)ethane) ligands.

During the last three decades, different palladium-fullerene complexes have been developed extensively as efficient catalysts for a variety of reactions due to their unique nanostructures and higher surface areas than traditional Pd-based catalysts.¹⁰⁻¹⁴ Sulman and Leszczynski first investigated the catalytic activity of η^2 -C₆₀Pd(PPh₃)₂ complex in the selective hydrogenation of acetylenic alcohols.^{10,12,14} Recently, the use of palladium catalysts supported on functionalized fullerenes (C₆₀) as potential nanomediators in the formation of C-C bonds has been also reported.¹⁵ The successful generation of such Pd–phosphine catalysts based on stabilized nanocarbons would provide a powerful tool for advanced organic synthesis.

The results from the studies mentioned above demonstrate clearly the possibility of using the palladafullerenes as nanocatalysts in the Mizoroki-Heck cross-coupling reaction which is one of the fundamental palladium(0)-catalyzed C-C bond-forming reactions. Although there are many examples of catalytic systems for the Heck reaction,¹⁶⁻¹⁸ the application of high-performance Pd nanoparticles as accessible, robust, and recyclable heterogeneous catalysts specially for aryl chlorides due to their low yield and long reaction times is still a challenge.¹⁹⁻²¹ Since aryl chlorides are relatively abundant and inexpensive, they are the most desirable substrates from an industrial point of view in Csp^2-Csp^2 cross coupling reactions.

As a part of our research program aiming at the investigation of fullerene-based carbon nanostructures,⁹ herein, we report the synthesis, characterization and application of new palladium(0)-[60]fullerene complexes systematically as heterogeneous nanocatalysts in the Mizoroki-Heck coupling reaction of unreactive aryl chlorides. Because of their electron-rich phosphine ligands and special nanostructures, they might be ideal candidates for the development of a unique class of heterogeneous catalysts. Furthermore, we turned our attention to a detailed study of the overall bonding modes in the palladafullerenes incorporating

phosphorus ylides of the type $Ph_2P(CH_2)_2PPh_2=C(H)C(O)R$ (R= $C_{10}H_7$ (**Y**¹), C_6H_4Cl (**Y**²)) acting in a terminal monodentate P-donor and/or a bidentate chelate P,C-donor mode, by NMR spectroscopy and DFT calculations.

Experimental

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General considerations

All manipulations were carried out under dry nitrogen using standard Schlenk techniques unless otherwise noted. Toluene and chloroform were used as reagent grade and dried over Na/benzophenone and P₂O₅, respectively. C₆₀ (+99.5%), Pd(dba)₂ and all other chemicals were purchased from commercial vendors and used without further purification. NMR spectra were recorded at the ambient temperature on Bruker Avance 400 MHz and 250 MHz instruments in CDCl₃ or DMSO-d₆ as solvents. Fourier transform IR spectra were recorded on a Shimadzu 435-U-04 spectrophotometer as KBr pellets, in the 200-4000 cm⁻¹ region.

Synthesis of phosphorus ylides

These compounds were prepared using a modified literature procedure.²² A solution of triethyl amine (0.5 mL) in toluene (1.0 mL) was added dropwise to a stirring solution of $[Ph_2P(CH_2)_2PPh_2CH_2C(O)C_{10}H_7]Br$ (323 mg, 0.5 mmol) in toluene (3.0 mL). The reaction mixture was stirred for an additional 20 min and then filtered off. The filtrate was concentrated to half the original volume and petroleum ether (10 mL) was added, resulting in formation of a yellow precipitate. The residue was collected by centrifugation and washed with additional petroleum ether (3 × 10 mL). The precipitate was dried *in vacuo* to afford a bright yellow powder. $Ph_2P(CH_2)_2PPh_2=C(H)C(O)C_{10}H_7$ (Y¹); Yield: 246 mg (87%), M.p. 142-144 °C. Selected IR absorption in KBr (cm⁻¹): 1577 (C=O). ³¹P NMR (162.15 MHz, CDCl₃) δ_P (ppm) -

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12.93 (d, PPh₂, ${}^{3}J_{P-P} = 47.99$ Hz), 16.88 (d, PCH, ${}^{3}J_{P-P} = 47.99$ Hz). ¹H NMR (400.62 MHz, CDCl₃) $\delta_{\rm H}$ (ppm) 2.81 (br, 2H, CH₂), 2.24 (br, 2H, CH₂), 4.30 (br, 1H, PCH), 7.23–8.05 (m, 27H, H_{ar}). ¹³C NMR (100.72 MHz, CDCl₃) $\delta_{\rm C}$ (ppm) 20.63 (d, PCH, ${}^{1}J_{P-C} = 71.31$ Hz), 126.57–142.09 (m, C_{ar}), 184.85 (s, CO). The ¹H and ³¹PNMR spectral data of Ph₂PCH₂PPh₂=C(H)C(O)C₆H₄Cl (**Y**²) matched those reported in the literature.²²

Synthesis of $[(\eta^2 - C_{60})Pd(Ph_2P(CH_2)_2PPh_2 = C(H)C(O)C_{10}H_7)_2]$ (1)

A solution of Pd(dba)₂ (0.029 g, 0.05 mmol) in toluene (3 mL) was added to a C₆₀ (0.036 g, 0.05 mmol) toluene solution being stirred, resulting in a black suspension by the end of the addition. A solution of phosphorus ylide (0.1 mmol) in toluene was then injected slowly into the resulting suspension. The reaction mixture was stirred for an additional 2h and consequently 30 mL of hexane was layered over the solution. Afterwards, the solid residue was triturated with diethyl ether twice to obtain the corresponding palladium(0)-[60]fullerene compound as a dark green solid. Yield: 70 mg (72%), M.p. > 300 °C. Selected IR absorption in KBr (cm⁻¹): 517 (C₆₀), 1573 (C=O). ³¹P NMR (101.25 MHz, CDCl₃) δ_P (ppm) 16.48 (d, PPh₂, ³J_{P-P} = 43.53 Hz), 17.52 (d, PCH, ³J_{P-P} = 44.55 Hz). ¹H NMR (250.13 MHz, CDCl₃) δ_H (ppm) 2.85 (m, 8H, CH₂), 4.23 (d, 2H, PCH, ²J_{P-H} = 22.51), 7.14–8.41 (m, 54H, H_{ar}). ¹³C NMR (62.90 MHz, CDCl₃) δ_C (ppm) 21.26 (m, CH₂), 47.45 (d, PCH, ¹J_{P-C} = 105.67 Hz), 124.85-134.16 (m, C_{ar}), 141.56-145.75 (m, C₆₀), 185.12 (s, CO).

Synthesis of $[(\eta^2 - C_{60})Pd(Ph_2P(CH_2)_2PPh_2 = C(H)C(O)C_6H_4Cl)_2]$ (2)

Yield: 64 mg (67%), M.p. > 300 °C. Selected IR absorption in KBr (cm⁻¹): 522 (C₆₀), 1578 (C=O). ³¹P NMR (101.25 MHz, CDCl₃) δ_P (ppm) 16.53 (d, PPh₂, ³J_{P-P} = 43.53 Hz), 17.35 (d, PCH, ³J_{P-P} = 43.53 Hz). ¹H NMR (250.13 MHz, CDCl₃) δ_H (ppm) 2.65 (m, 8H, CH₂), 4.08 (t,

2H, PCH, ${}^{2}J_{P-H} = 22.51$), 7.13–7.86 (m, 48H, H_{ar}). ${}^{13}C$ NMR (62.90 MHz, CDCl₃) δ_{C} (ppm) 21.64 (m, CH₂), 47.17 (d, PCH, ${}^{1}J_{P-C} = 108.82$ Hz), 128.46-133.35 (m, C_{ar}), 142.23-144.88 (m, C₆₀), 184.09 (s, CO).

General procedure for Mizoroki-Heck reaction. In the presence of air, a vial was charged with aryl chloride (1 mmol), styrene or ethyl acrylate (1.5 mmol), K_2CO_3 (1.5 mmol) and Pd catalyst (0.001 mol%) in methanol (2 ml). The reaction mixture was stirred for the required period of time at 60 °C to complete the reaction, as monitored by TLC. After being cooled to ambient temperature, the mixture was extracted with n-hexane (15 ml). The organic layer was then dried over CaCl₂ and evaporated under the reduced pressure to give a crude product analyzed by ¹H and ¹³C NMR spectroscopy.

Results and discussion

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Synthesis and characterization

A toluene solution of phosphorus ylides \mathbf{Y}^1 and \mathbf{Y}^2 reacted with $[C_{60}Pd_x]$, which is achieved by in-situ reaction of C_{60} and $Pd(dba)_2$, afforded new monodentate P-coordinated complexes $[(\eta^2 - C_{60})Pd(\mathbf{Y}^1)_2]$ (1) and $[(\eta^2 - C_{60})Pd(\mathbf{Y}^2)_2]$ (2) (Scheme 2). Other possible side products such as P, Ccoordinated $[(\eta^2 - C_{60})Pd(\kappa^2 - \mathbf{Y}^1)]$ and $[(\eta^2 - C_{60})Pd(\kappa^2 - \mathbf{Y}^2)]$ complexes have not been observed in the reactions, as evidenced by spectroscopic analysis. The palladium-fullerene complexes can be precipitated as a result of slow diffusion of hexane into the obtained toluene solution. In contrast to phosphorus ylides incorporating dppm (1,2-Bis(diphenylphosphino)methane) ligands, which is able to form five membered P, C-coordinated complexes with fullerenes, the formation of six membered P, C-coordinated complexes of dppe (1,2-Bis(diphenylphosphino)ethane) ones was not favorable.⁹ This may be due to the ring strain effect in six-membered complexes of $[(\eta^2 -$

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 C_{60} Pd(κ^2 -Y)] type on one hand and as a result of further attack of free PPh₂ of diphosphine ligands on the other hand, leading to formation of P-coordinated complexes [(η^2 -C₆₀)Pd(Y)₂]. Based on the known chemistry of palladium(0)-[60]fullerene complexes,²³⁻²⁷ an implicit mechanism for the formation of these complexes is proposed (Scheme 2).



Scheme 2. Proposed pathway for the synthesis of complexes 1 and 2.

The structure of products was fully corroborated by Fourier transform infrared (FT-IR), ¹H, ¹³C and ³¹P NMR spectroscopy. Further conventional techniques such as scanning electron microscopy (SEM), inductively coupled plasma optical emission spectroscopy (ICP-OES), transmission electron microscopy (TEM), thermogravimetry (TGA) and energy-dispersive X-ray spectroscopy (EDX) were also used for the characterization of the new nanocatalyst $[(\eta^2 - C_{60})Pd(Y^1)_2]$ (1).

According to the scheme 2, the reaction of polymeric complex $C_{60}Pd_n$ with either the phosphorus ylides \mathbf{Y}^1 or \mathbf{Y}^2 leads to the η^1 -P-coordinated palladium(0)-fullerene complexes 1 and 2, respectively, without any evidence of by-product formation. In contrast to the ¹H and ¹³C NMR signals, the ³¹P resonances are usually broad and sensitive to even relatively small variations in the chemical environment around the phosphorus atoms of the complexes. The ³¹P{¹H} NMR spectrum of complex 1 features two doublets at 16.48 and 17.52 ppm, shifted downfield from that of \mathbf{Y}^1 (-12.93 and 16.88 ppm) due to the coordination of the ylides to palladium through the free phosphine groups. Similarly, the ³¹P signal splitting of two phosphorus atoms at 16.53 and 17.35 ppm suggests that the coordination of the ylides has occurred in the complex 2. The smaller downfield shifts for the both of PPh₂ and PCH phosphorus atoms in AB pattern compared to those of the AX system in bidentate phosphorus based complexes, ^{9,22,28} indicate the η^1 -P-coordinated mode of phosphorus ylides in the palladium(0)-fullerene complexes 1 and 2.

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The ¹HNMR spectra of the complexes **1** and **2** in CDCl₃ each exhibit one broad peak due to the one P-bound CH group at 4.23 and 4.08 ppm, respectively, revealing the C_{sp}^2 -P bond in these complexes. Furthermore, no significant changes in resonance values were observed for the ylidic protons after complexation, which is in agreement with the P-coordination character of the ylides in these complexes. The presence of the carbonyl group in the P-chelated palladium(0) complexes **1** and **2** is also confirmed by ¹³C{¹H} NMR spectroscopy displaying signals at 185.12 and 184.09 ppm, respectively, which remained unaffected compared to the parent ylides **Y**¹ and **Y**² (184.85 and 183.91 ppm, respectively). The IR spectra of complexes **1** and **2** both demonstrate a sharp v (C=O) band at 1573 and 1578 cm⁻¹, respectively. These unchanged absorption bands compared to the v (C=O) stretching bands of their precursors **Y**¹ (1577 cm⁻¹) and **Y**² (1579 cm⁻¹) suggest that the coordination of the ylides occurs only through the PPh₂

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groups. Furthermore, the IR spectra of both complexes display four active bands of C_{60} around 522, 579, 1184 and 1435 cm⁻¹. Therefore, the spectroscopic data lend support to the monodentate η^1 -P-coordination in complexes **1** and **2** of their overall bonding modes.

For investigating the size and surface morphology of the prepared catalysts, SEM images of C_{60} and palladium(0)-[60]fullerene complex **1** were obtained as shown in Figure 1. The particles were so strongly aggregated that discrete particles were impossible to find and average particle size was difficult to obtain. However, the agglomerated particles were dispersed in SEM image of complex **1** having similar or close crystallographic orientations. As depicted in Figure 1, the catalyst particle sizes which labelled in the SEM image are in the range 43.3- 81.0 nm.



Fig. 1. SEM photographs of (a) C_{60} , and (b) Palladium(0)-[60] fullerene complex 1.

TEM study provides further insights into the morphology and nanometer scale of the prepared catalyst **1**. The results revealed that the palladium particles were homogeneously deposited on the surfaces of the supporting modified-fullerenes. Furthermore, the presence of spherical Pd nanoparticles is clearly distinguished as dark spots in Figure 2, with a mean particle diameter of

approximately 22.05 nm. TEM images show that the fullerene-functionalized palladium nanoparticles possess almost spherical morphology with relatively good monodispersity.



Fig. 2. TEM images of palladium(0)-[60]fullerene complex 1.

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The EDX measurements evidence the presence of all individual elements as expected. Elemental spectrum determined from the EDX analysis is shown in Figure 3, which demonstrates the presence of palladium, phosphorus, oxygen and carbon in the palladium nanostructure **1**. Also, to obtain an insight into the accurate amount of Pd in prepared catalysts, the ICP-OES analysis has been applied. According to the ICP analysis, the palladium content in complexes **1** and **2** has been determined 5.24 and 5.30 wt%, respectively.



Fig. 3. EDX analysis of palladium(0)-[60]fullerene complex 1.

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In order to investigate the thermal stability of the new nanocatalyst **1**, TG analysis was conducted in an inert atmosphere. As shown in Figure 4 (a), for C₆₀, the light mass loss (3.7 wt%) below 250 °C can be attributed to the evaporation of absorbed solvents such as water. A thermal decomposition starting after 380 °C, with a weight loss of about 96%, can be assigned to carbon cage and amorphous carbon decompose in fullerene. For C₆₀-Pd(0) complex **1** (Figure 4 (b)), the heating of the compound from 300 °C to 480 °C resulted in 30.7% weight loss, mainly due to the removal of phosphorus-containing functional ligand. The second weight loss occurs at temperature range of 500-660 °C which is related to the decomposition of fullerene (C₆₀). Therefore, the amount of palladium on the surface of the supporting modified-fullerene is estimated to be 25.1% from the TG analysis.



Fig. 4. TGA spectra of (a) C_{60} , and (b) Palladium(0)-[60]fullerene complex 1

Mizoroki-Heck coupling reaction

Following on initial work,⁹ further improvement in catalytic system design triggered the use of new palladafullerene complexes for the Mizoroki–Heck reaction. The reaction of economical aryl chlorides and olefines such as styrene and electron-deficient ethyl acrylate is presented for catalytic performance evaluation of the Pd catalysts. Some starting materials of the optimized catalyst systems, mentioned in Table 1, are reported as a model.

Table 1. Selected experimental results ^a .						
C ₂ H	+	CI	Catalyst Methanol, 60 °C K_2CO_3	C ₂ H ₅ O	R	
3a: Styrene 3b: Ethyl acrylate		4a : R= NO ₂ 4b : R= H 4c : R= OCH ₃		5		
Entry	cat. loading [mol %]	Olefin	Aryl chloride	Catalyst	Yield $[\%]^b$	
1	0.01	3 a	4 a	1 2	90 94	
2	0.01	3 a	4b	1 2	95 93	
3	0.01	3 a	4c	1 2	92 93	
4	0.01	3b	4a	1 2	90 93	
5	0.01	3b	4b	1 2	91 91	
6	0.01	3b	4c	1 2	88 91	
7	0.001	3 a	4a	1 2	93 92	
8	0.001	3 a	4b	1 2	92 90	
9	0.001	3 a	4c	1 2	91 89	
10	0.001	3b	4a	1 2	89 90	
11	0.001	3b	4b	1 2	86 88	
12	0.001	3b	4c	1 2	85 88	

^a Reaction conditions for Mizoroki–Heck coupling reaction: 3 (1.5 mmol), 4 (1 mmol), K₂CO₃ (1.5 mmol), methanol (2 mL), 60 °C and catalysts 1 and 2.
^b yield of isolated product (5).

 $[(\eta^2 -$ Indeed. initial optimized conditions involved our C_{60} Pd(Ph₂P(CH₂)₂PPh₂=C(H)C(O)C₁₀H₇)₂] (1) as the palladium nanocatalyst and K₂CO₃ as base. However, the difference between bases was less pronounced under the optimized conditions, and thus, K₂CO₃ was chosen as inexpensive and readily available inorganic base (Table 2). Subsequently, the effect of different solvent systems was also investigated in the reaction. The reactions were conducted using methanol which provides the heterogeneous condition for the methanol-insoluble catalyst, with respect to the high catalyst recovery, product isolation, and recycling. It is inferred that the fullerene-functionalized palladium nanoparticles as nanocatalysts display elevated catalytic properties compared to the classical catalysts. Under the same conditions, similar catalytic activities were observed using 0.001 mol% of $[(\eta^2 C_{60}$ Pd(Ph₂P(CH₂)₂PPh₂=C(H)C(O)C₆H₄Cl)₂] (2) with high efficiency for the reactions described above (Table 1).

Table 2. Optimization of base and solvent for Heck cross-coupling reaction of 1-chloro-4-methoxybenzene with styrene a^{a} .

+ Cl						
Entry	Base	Solvent	Temp (°C)	Time (h)	Isolated yield (%)	
1	Na ₂ CO ₃	methanol	60	10	82	
2	K_2CO_3	methanol	60	3	91	

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3	Cs_2CO_3	methanol	60	2	90		
4	NaOAc	methanol	60	10	77		
5	K_2CO_3	DMF	120	4	90		
6	K_2CO_3	NMP	140	4	86		
7	K ₂ CO ₃	dioxane	100	9	78		
^a Reacti	on conditions:	1-chloro-4-methoxy	ybenzene (1 mn	nol), Styrene (1.5	5 mmol), base (1.5		
mmol) and 2 ml solvent.							

It is demonstrated that switch from palladium(II)- to palladium(0)-complexes for Csp^2-Csp^2 bondforming reactions allows the use of recoverable catalysts for several times, while retaining high productivity and stability (Figure 5). Neither of heterogeneous nanocatalysts showed considerable loss of activity after five cycles. Leaching experiments were performed to examine the stability of the Pd nanoparticles. After the first run, ICP analysis showed that the amount of palladium leached out into the solvent was only 1.16 ppm for **1** and 1.20 ppm for **2**. There were no Pd leachings detected for these catalysts after the first and second recycles. Besides, after three hours for both runs, removed were the catalysts from the solutions and the reactions were continued for three hours, while the conversion of styrene to chlorobenzene remained unchanged implying that there were no contributions from palladium leached into reaction solutions. The concentrations of palladium residue in the solutions were found to be 1.80 and 2.08 ppm for catalyst **1** and 1.52 and 2.01 ppm for catalyst **2** after the fourth and fifth runs, respectively. Based on the ICP analysis, the slight loss of reactivity was ascribed to metal leaching over the successive reuses.

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As shown in Figure 6, the structure of the reused nanocatalyst was investigated *via* IR spectra, confirming the truly heterogeneous nature of the catalyst. Although the aryl chlorides bearing

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electron-withdrawing groups react more slowly than electron-donating ones, the conversion of both aryl chlorides represent the desired products in high yields.



Fig. 5. Recycling of the catalysts 1 and 2 in the Heck reaction of chlorobenzene with styrene in methanol at 60 °C.



Fig. 6. FTIR spectra of (a) Y^1 , (b) fresh and (c) used Palladium(0)-[60]fullerene catalyst 1.

Further decrease in catalyst loading down to 0.001 mol% and also increasing in the scale of reaction by a factor of 10 without significant difference in catalytic performance, make them

promising for efficient upscaling and advanced applications. Another clear advantage of using the prepared palladium(0)-[60]fullerenes instead of corresponding palladium(II) complexes ²⁹ as catalysts for the Heck reactions is the fact that the latter require reduction of palladium(II) by oxidation of a phosphorus atom as a preactivation step to generate the Pd(0) active species.³⁰ These results may confirm the validation of our initial choice to concentrate on the modification of the Pd(II)-based catalysts substituent.

Theoretical studies

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As a continuation of our previous work,⁹ DFT computational studies were carried out to explore the nature of metal-ligand bonds in $(\eta^2-C_{60})Pd(Y^1)$ and $(\eta^2-C_{60})Pd(Y^1)_2$ complexes in more details. So, it used DFT calculations at B3LYP/6-31G*/LANL2MB level of theory using the Gaussian 09 program for optimization of the complexes.³¹ The optimized structures of $(\eta^2-C_{60})Pd(Y^1)$ and $(\eta^2-C_{60})Pd(Y^1)_2$ complexes are shown in Figure 7. Also in Supporting Information the Cartesian atomic coordinates of both compounds are available. It is notable that in these complexes the Pd atom can be coordinated to two different types of C–C bonds in the C_{60} structure; the bonds at the junction of two hexagons, [6,6]-bonds, and those between one pentagon and one hexagon [5,6]-bonds. In this work, the same as our previous work and based on experimental observations for similar complexes,^{9, 32} we have assumed the Pd atom to be only attached to a [6,6]-double bond.



Fig. 7. The optimized structures of $(\eta^2-C_{60})Pd(Y^1)$ and $(\eta^2-C_{60})Pd(Y^1)_2$ complexes calculated by B3LYP-6-31G*/LANL2MB basis set.

Based on DFT calculations at BP86-D3/TZP level of theory, Energy decomposition analysis (EDA) was performed to study the theory values of the palladium– C_{60} and palladium– Y^1 bond energies in (η^2 - C_{60})Pd(Y^1) and (η^2 - C_{60})Pd(Y^1)₂ complexes. The EDA decomposes the interaction energy between two considered fragments A and B into four terms which can be interpreted in a chemically meaningful way. The four terms are including the quasiclassical electrostatic interaction between the frozen charges of the fragments (ΔE_{elec}); the exchange (Pauli) repulsion between electrons possessing the same spin (ΔE_{Pauli}); the orbital interaction term (ΔE_{orb}) and the dispersion contributions (ΔE_{disp}).

The EDA results are obtained by DFT calculation and collected in Table 3. The interaction energy values, ΔE_{int} , between (η^2 -C₆₀)Pd and phosphorus ylide (**Y**¹) fragments are somewhat

larger than those between (η^2-C_{60}) and Pd–phosphorus ylide (Y¹) fragments. As can be seen, the percentage contribution of ΔE_{elec} term in the series of studied complexes is in the range of 52-57% for (η^2-C_{60}) Pd-Y and 53-54% for (η^2-C_{60}) -PdY bond. Indeed, in these complexes and for both (η^2-C_{60}) -PdY and (η^2-C_{60}) Pd–Y bonds the contribution of ΔE_{elec} term in total interaction energy is larger than ΔE_{orb} term.

Table 3. Energy decomposition analysis (EDA) data [kcal/mol] at BP86-D3/TZP//B3LYP-6-31G*/LANL2MB level of theory.

Complexes	Fragments	ΔE_{int}	ΔE_{Pauli}	ΔE _{elec}	ΔE _{orb}	ΔE_{disp}
$(m^2 C)$ D $d(V^1)$	$(\eta^2 - C_{60})Pd(Y^1)$	-86.31	129.25	-123.09(57%)	-71.42(33%)	-21.05(10%)
$(\eta - C_{60})$ Pa(Y)	$(\eta^2 \text{-} C_{60})Pd(Y^1)$	-69.87	189.13	-140.14(54%)	-98.55(38%)	-20.31(8%)
$(m^2 C)$) $\mathbf{P}_{\mathbf{J}}(\mathbf{V}^1)$	$(\eta^2 - C_{60})Pd(Y^1)_2$	-93.55	90.23	-96.38(52%)	-52.90(29%)	-34.50(19%)
$(\eta - C_{60})$ Pa $(Y)_2$	$(\eta^2 - C_{60}) Pd(Y^1)_2$	-78.43	206.86	-151.13(53%)	-109.57(38%)	-24.59(9%)

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In accordance with the spectroscopic results, it is demonstrated that the ylide (\mathbf{Y}^1) acted in a terminal monodentate P-donor mode to form P-coordinated complex. The calculated values for interaction energy are consonant with the above observation. As can be seen in Table 3, the value of interaction energy between (η^2 -C₆₀)Pd and Y^1 in (η^2 -C₆₀)Pd(Y^1)₂ complex (-93.55 kcal/mol) is larger than that between (η^2 -C₆₀)Pd and Y^1 in (η^2 -C₆₀)Pd(Y^1) (-86.31 kcal/mol). Thus, two P-coordinated Y^1 molecules in (η^2 -C₆₀)Pd(Y^1)₂ complex have a larger interaction with (η^2 -C₆₀)Pd than one P, C-coordinated Y^1 molecule. In another word, the P-complexation with C₆₀ or linear product seems to be more probable and more stronger than bidentate P, C-chelation with C₆₀. Additionally, more experiments were done to confirm the above results and the following reaction was studied by theoretical calculations.

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$$(\eta^2 - C_{60})Pd(Y^1) + Y^1 \rightarrow (\eta^2 - C_{60})Pd(Y^1)_2 \quad \Delta E = -9.16 \text{ kcal/mol}$$

As is clearly shown, the formation of P-coordinated $(\eta^2-C_{60})Pd(Y)_2$ complex by addition of ylide Y^1 to P, C-coordinated $(\eta^2-C_{60})Pd(Y^1)$ complex with negative value for differences energy, ΔE , is exothermic which can be done spontaneously. These results suggest that the $(\eta^2-C_{60})Pd(Y^1)_2$ complex with two ligands behave as monodentate P-donors highly supported by the data of NMR spectroscopy.

The visualization of the electron distribution in various orbitals at different electronic states, e.g. HOMO, HOMO-1, LUMO, and LUMO+1 for $(\eta^2-C_{60})Pd(Y^1)$ and $(\eta^2-C_{60})Pd(Y^1)_2$ complexes was also evaluated by DFT calculations (Figure 8). It is intuitive that the HOMOs distribution of the $(\eta^2-C_{60})Pd(Y^1)$ and $(\eta^2-C_{60})Pd(Y^1)_2$ complexes, as expected, is essentially situated on palladium-ylide moiety while LUMO and LUMO+1 are located on the C_{60} entity as an acceptor molecule. Fullerenes, as excellent π -acceptor molecules, differ from other acceptor molecules with well-known features in terms of their larger size, spherical shape, high symmetry, unique electronic structure, and polarizability. In donor-acceptor dyad systems with C_{60} , like the current study, fullerenes act as acceptor molecules.



Fig. 8. HOMOs and LUMOs of (η²-C₆₀)Pd(Y) (top) and (η²-C₆₀)Pd(Y)₂ (bottom) complexes in various electronic states, e.g., (a) HOMO, (b) HOMO-1, (c) LUMO, (d) LUMO+1 done by DFT/B3LYP/6-31G* calculations.

Conclusion

The present study combines the organo-fullerene chemistry with the phosphine-based Pd catalytic systems to report the new palladium(0)-[60]fullerene complexes as efficient nanocatalysts for Mizoroki-Heck cross-coupling reaction. The high activity and enhanced stability of the catalysts can be attributed to the nature of palladium-based nanoparticles and the bulky diphosphine ligands. On the other hand, a simple preparation procedure of the reusable nanocatalysts and the high catalytic performance for unreactive aryl chlorides with low catalyst loading were recognized as their most influential factors. Based on the spectroscopic results, the exclusive formation of P-coordinated (η^2 -C₆₀)Pd(Y)₂ complexes was achieved using appropriate phosphonium ylides. DFT calculations also confirmed that the terminal monodentate P-donor mode of applied phosphonium ylides is more stable than the bidentate chelate P,C-donor mode in complexes **1** and **2**. This promising field will go on further to elucidate the steric and electronic factors for the binding energy of bifunctional diphosphine-based ligands on metallofullerene surfaces that influence their catalytic activity in other types of coupling reactions.

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Notes and references

- H.W. Kroto, J.R. Heath, S.C. O'Brien, R.F. Curl, R.E. Smalley, *Nature*, 1985, **318**, 162–163.
- 2 (a) A. V. Usatov, E. V. Martynova, I. S. Neretin, Y. L. Slovokhotov, A. S. Peregudov and
 Y. N. Novikov, *Eur. J. Inorg. Chem.* 2003, 2003, 2041-2044. (b) S. Burghardt, A. Hirsch,

B. Schade, K. Ludwig and C. Böttcher, *Angew. Chem. Int. Ed.* 2005, 44, 2976-2979. (c)
P. Compain, C. Decroocq, J. Iehl, M. Holler, D. Hazelard, T. Mena Barragán, C. Ortiz
Mellet and J. F. Nierengarten, *Angew. Chem.* 2010, 122, 5889-5892. (d) J.-F.
Nierengarten, J. Iehl, V. Oerthel, M. Holler, B. M. Illescas, A. Muñoz, N. Martín, J. Rojo,
M. Sánchez-Navarro and S. Cecioni, *Chem. Commun.* 2010, 46, 3860-3862.

- 3 (a) A. Ramírez-Monroy and T. M. Swager, *Organometallics*, 2011, 30, 2464-2467. (b) A. Krueger, *Carbon materials and nanotechnology*, John Wiley & Sons, 2010. (c) C.-Z. Li, Y. Matsuo and E. Nakamura, *J. Am. Chem. Soc.* 2010, 132, 15514-15515. (d) D. V. Konarev, S. S. Khasanov, S. I. Troyanov, Y. Nakano, K. A. Ustimenko, A. Otsuka, H. Yamochi, G. Saito and R. N. Lyubovskaya, *Inorg. Chem.* 2013, 52, 13934-13940.
- 4 F. Langa and J.-F. Nierengarten, *Fullerenes: principles and applications*, Royal Society of Chemistry, 2007.
- 5 B. C. Thompson and J. M. Fréchet, Angew. Chem. Int. Ed. 2008, 47, 58-77.
- 6 M. A. Lebedeva, T. W. Chamberlain and A. N. Khlobystov, *Chem. Rev.* 2015, **115**, 11301-11351.
- 7 M. Halim, R. D. Kennedy, S. I. Khan and Y. Rubin, Inorg. Chem. 2010, 49, 3974-3976.
- 8 A. L. Balch and K. Winkler, *Chem. Rev.* 2016, **116**, 3812-3882.

Published on 25 July 2017. Downloaded by Newcastle University on 26/07/2017 07:41:47.

- 9 S. J. Sabounchei, M. Hosseinzadeh, A. Hashemi, S. Salehzadeh and F. Maleki, *Dalton Trans.* 2016, 45, 13899-13906.
- 10 E. Sulman, V. Matveeva, N. Semagina, I. Yanov, V. Bashilov and V. Sokolov, J. Mol. Catal. A: Chem. 1999, 146, 257-263.
- 11 N. F. Goldshleger, Fullerene Sci. Technol. 2001, 9, 255-280.

- 12 I. Yanov, J. Leszczynski, E. Sulman, V. Matveeva and N. Semagina, Int. J. Quantum Chem. 2004, 100, 810-817.
- 13 E. V. Starodubtseva, V. I. Sokolov, V. V. Bashilov, Y. N. Novikov, E. V. Martynova, M. G. Vinogradov and O. V. Turova, *Mendeleev Commun.* 2008, 18, 209-210.
- 14 Q. Zhang, Z. Bai, M. Shi, L. Yang, J. Qiao and K. Jiang, *Electrochim. Acta.* 2015, 177, 113-117.
- 15 H. Veisi, R. Masti, D. Kordestani, M. Safaei and O. Sahin, *J. Mol. Catal. A: Chem.* 2014, 385, 61-67.
- 16 I. P. Beletskaya and A. V. Cheprakov, Chem. Rev. 2000, 100, 3009-3066.
- 17 Y.-C. Lin, H.-H. Hsueh, S. Kanne, L.-K. Chang, F.-C. Liu, I. J. Lin, G.-H. Lee and S.-M. Peng, *Organometallics*, 2013, **32**, 3859-3869.
- 18 M. R. Smith, Y. J. Jang, J. Y. Kim and M. A. Ciufolini, *Tetrahedron*, 2013, **69**, 10139-10151.
- F. Giacalone, V. Campisciano, C. Calabrese, V. La Parola, Z. Syrgiannis, M. Prato and M. Gruttadauria, ACS nano, 2016, 10, 4627-4636.
- 20 A. F. Panahi, N. Zarnaghash and A. Khalafi-Nezhad, New J. Chem. 2016, 40, 1250-1255.
- 21 R. Li, R. Li, C. Wang, L. Gao and Q. Chen, Dalton Trans. 2016, 45, 539-544.
- 22 S. J. Sabounchei, S. Samiee, D. Nematollahi, A. Naghipour and D. Morales-Morales, *Inorg. Chim. Acta*, 2010, **363**, 3973-3980.
- 23 S. A. Lerke, B. Parkinson, D. H. Evans and P. J. Fagan, J. Am. Chem. Soc. 1992, 114, 7807-7813.
- 24 H. Nagashima, Y. Kato, H. Yamaguchi, E. Kimura, T. Kawanishi, M. Kato, Y. Saito, M. Haga and K. Itoh, *Chem. Lett.* 1994, 23, 1207-1210.

- 25 V. Sokolov, Russ. J. Coord. Chem. 2007, 33, 711-724.
- 26 V. V. Bashilov, F. M. Dolgushin, P. V. Petrovskii, V. I. Sokolov, M. Sada, T. Benincori and G. Zotti, *J. Organomet. Chem.* 2005, **690**, 4330-4336.
- 27 L.-C. Song, G.-A. Yu, Q.-M. Hu, C.-M. Che, N. Zhu and J.-S. Huang, J. Organomet. Chem. 2006, 691, 787-792.
- 28 S. J. Sabounchei, M. Panahimehr, M. Hosseinzadeh, R. Karamian, M. Asadbegy and A. Masumi, J. Mol. Struct. 2014, 1061, 90-96.
- 29 (a) S. J. Sabounchei and M. Ahmadi, *Inorg. Chim. Acta*, 2013, 405, 15-23. (b) S. J. Sabounchei and M. Hosseinzadeh, *J. Chem. Sci.* 2015, 127, 1919-1926.
- 30 C. Allolio and T. Strassner, J. Org. Chem. 2014, 79, 12096-12105.
- 31 M. Frisch, Inc.: Wallingford, CT, 2009.

32 (a) L.-C. Song, F.-H. Su and Q.-M. Hu, *J. Org. Chem.* 2005, **690**, 1121-1124. (b) L.-C. Song, G.-F. Wang, P.-C. Liu and Q.-M. Hu, *Organometallics*, 2003, **22**, 4593-4598.

Monodentate palladium(0)-[60]fullerene complexes of diphosphine ligands as efficient and sustainable nanocatalysts for Mizoroki-Heck coupling reaction of aryl chlorides

Seyyed Javad Sabounchei^{a*}, Marjan Hosseinzadeh^a, Morteza Zarepour-jevinani^b

and Bahram Ghanbari^b

^a Faculty of Chemistry, Bu-Ali Sina University, Hamedan,65174, Iran

^b Department of Chemistry, Sharif University of Technology, PO Box 11155-3516, Tehran, Iran



The present article combines fullerene chemistry with phosphine-based Pd catalytic systems to report the new palladium(0)-[60]fullerene complexes as heterogeneous nanocatalysts for carbon–carbon bond transformations of unreactive aryl chlorides.

^{*} Corresponding author. E-mail address: jsabounchei@yahoo.co.uk (S.J. Sabounchei).