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Support-free Pd₃Co NCs as an efficient heterogeneous nanocatalyst for novel organic transformations of C-C coupling reactions

Samjhana Pradhan, Kanchan Mishra and Yong Rok Lee*

Dedication ((optional))

Abstract: A support-free heterogeneous Pd₃Co nanostructured composite (NC), synthesized via hydrothermal route, acted as an effective catalytic system in multivariate Heck, Sonogashira and Suzuki-type coupling reactions of iodonium ylides. The XPS analysis of the bimetallic Pd₃Co NCs confirmed the elemental composition as 75% palladium and 25% cobalt. Furthermore, HRTEM analysis confirmed the spherical morphology of Pd₃Co bimetallic nanoparticles. The average diameter of the NCs is 14.8 nm. The coupling reaction proceeded via the generation of a-iodoenones with simultaneous migration of the phenyl group thereby giving a scaffold with higher atom economy. The heterogeneous Pd_3Co NCs were recycled and reused without any significant change in catalytic ability, for up to five reaction cycles. The high concentration of Pd content and association of cobalt into the lattice of palladium appears to enhance its catalytic ability for the diverse coupling reactions in comparison with its monometallic counterparts as well as bimetallic NCs with comparatively lesser amount of Pd.

Introduction

C-C bond formation is one of the most important processes in synthetic organic chemistry. The most common and well-known types are Suzuki,^[1-3] Heck,^[4,5] Sonogashira coupling reactions,^[6] and so on. These provide facile and highly efficient route for the synthesis of natural products, polymers, ^[7,8] agrochemicals and pharmaceuticals. ^[9,10] Since its discovery innumerable methods have been reported for coupling reactions with burgeoning use of palladium bimetallic nanostructured composites. The synergistic effect imparted by the bimetallic nanostructured composites (NCs) due to their tunable components and morphologies have attracted significant interest in the field of catalysis. The latter is attributed to the electronic interaction that interplays between the two metal atoms. ^[11,12]

Various studies have revealed that the incorporation of cheap as well as easily available 3d – transition metals with Pd to form Pd-M NCs (M = Co, Fe, Cu, Ni)^[13-17] is one of the most efficient approaches to increase the catalytic activity and utilization of Pd metal.^[18] In this context, Pd-Co bimetallic NCs have shown remarkable performance as heterogeneous nanostructured catalyst in coupling reactions. Shaaboni et al.,

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^[19a] Dabiri et al. ^[19b] and Xu et al. ^[19c] have reported separately on the synthesis of Pd-Co bimetallic NCs with graphene as a support material for Sonogashira and Suzuki reactions. However, the preparation of such supported nanostructured catalysts involves complicated multistep synthesis procedures. ^[20] In addition, the catalytic behaviour of the supported nanostructured catalysts is affected by various factors, such as, choice of support materials, particle size and preparation methods. ^[21a] Nonetheless, such kind of effects are negligible in support-free nanostructured composites, and henceforth, these are still considered as an important facet in the field of heterogeneous catalysis. ^[22]



Scheme 1. Synthesis of Pd_3Co NCs via hydrothermal route and their catalytic application as C-C coupling of iodonium ylides.

A number of studies have been reported previously on the synthesis of naked/ unsupported nanostructured particles (NPs) for organic reactions ^[21b-21d]. Zhang et al. ^[22] and Ordomsky et al. ^[23] have recently designed naked IrO₂ NPs and unsupported Ru NPs for hydrogenation of nitrogen heterocycles and amination of alcohol, respectively. In this case, the NPs were reported to exhibit high selectivity and stability without loss of activity or metal leaching. The support-free nanostructured catalyst possesses large number of free metallic surface sites that provides a platform rendering the catalytic activity more feasible by the elimination of support effect. ^[24] Similarly, our group have also previously designed transition metal based bimetallic

nanoparticles. These heterogeneous composites proved to be highly effective catalyst for various organic transformations. ^[25] Based on these approaches, herein, we have developed a facile and green approach for the one pot synthesis of support-free, palladium rich bimetallic Pd₃Co NCs via a hydrothermal method using ethylene glycol as a mild reducing agent (Scheme 1).

 Pd_3Co NCs have been used mostly to enhance the rechargeability of Li-O₂ cell, ^[26a] for oxygen reduction reaction on Li-O₂ cathode cell, ^[26b] and as hydrogen storage material. ^[26c] However, reports on the use of support-free Pd_3Co NCs as a catalyst in organic transformations are rarely known. In this regard, we have attempted to use Pd_3Co NCs as a catalyst for a variety of coupling reactions of iodonium ylides.



Scheme 2. Reported and novel strategies for the C-C coupling reactions of iodonium ylides.

lodonium ylides comprise an important branch of organic hypervalent iodonium chemistry. ^[27] They are widely used as analogues of the corresponding diazo compounds ^[28] and are highly resourceful compounds in organic synthesis. ^[29] Recently, direct cyclization of iodonium ylides with tertiary aryl amines for *N*-heterocycles has been reported by Wang group (Scheme 2a). ^[30] In addition, Takemoto and co-workers have demonstrated the Umpolung alkylation of silyl enol ethers with iodonium ylides (Scheme 2b). ^[31] However, direct coupling reactions of such iodonium ylides are relatively unknown. In 2002, Yang and coworkers reported the Pd-catalyzed reaction of iodonium ylides with aryl boronic acids for the synthesis of 3-aryl-4hydroxycoumarins (Scheme 2c).^[32] In this case, coupled products via simultaneous migration of the phenyl group were not observed. To the best of our knowledge, there have been no reports of transition metal-catalyzed or nanocatalyzed phenyl migration and direct coupling reactions of iodonium ylides for the construction of diverse organic compounds with higher atom economy. The present work is the first of its kind to synthesize support-free Pd₃Co NCs for the simultaneous phenyl migration and direct Heck-, Sonogashira-, and Suzuki-type coupling reactions of iodonium ylides with acrylates, arylalkynes, and boronic acids, respectively (Scheme 2d–2f).

Results and Discussion

Synthesis of Pd₃Co NCs

 Pd_3Co NCs were synthesized via one pot hydrothermal method using palladium(II) acetate and cobalt(II) acetate tetrahydrate as the metal precursors, and ethylene glycol as the reducing agent. The hydroxyl groups of ethylene glycol reduced the Pd^{2+} and Co^{2+} to its respective metallic forms, forming Pd_3Co NCs.

Characterization of Pd₃Co NCs

To identify the crystalline phase and composition of $Pd_3Co NCs$, XRD patterns of the catalysts were obtained (Figure 1a). They displayed typical Pd face-centred cubic (fcc) features without separate individual peaks for cobalt and its oxide. ^[33] The diffraction peaks corresponding to (111), (200), and (220) planes are consistent with those of pure Pd metals with an fcc structure (JCPDS no. 46-1043). The shift in the peak positions, compared to that of pure Pd, is subtle resulting in a bimetallic composition with small lattice contraction. ^[34] As the nanocomposites were not treated at high temperatures, a prominent shift in the relative peak angle did not occur.



Figure 1. (a) XRD patterns (inset: high resolution peak), (b) XPS peaks of Pd_3Co , PdCo, and Pd, (c) Survey scan, inset: atomic percentage of Pd and Co in Pd_3Co NCs, and (d) Co 2p electrons of Pd_3Co NCs.

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XPS studies of support-free Pd₃Co NCs were carried out to determine the elemental composition of the nanocatalyst and the valence state of the metals in the nanoparticles. The XPS spectra over a full range scan revealed the presence of Pd, Co, and Oxygen, with an elemental composition of Pd and Co as 75% and 25% (Figure 1c). The high resolution XPS spectrum of the Pd 3d was deconvoluted into Pd $3d_{5/2}$ and Pd $3d_{3/2}$ peaks. Each subshell exhibits two different valence states. i.e. Pd²⁺ and Pd⁰. The characteristic peaks at 335.2 and 340.5 eV explain the presence of metallic Pd in the nanocomposites with a spin orbit coupling constant at 5.3 eV. While the peaks observed at 337.2 and 342.4 eV can be attributed to the presence of a small amount of Pd (II) in the catalyst (Figure 1b). Similarly, the peak at 797.4 and 781.5 eV confirmed the formation of Co (0) in the NCs (Figure 1d). Furthermore, we have compared the XPS spectra of PdCo and Pd with that of the Pd₃Co NCs. The peak shifting towards the higher binding energies, with decrease in cobalt content, indicate the synergistic effect of Pd with Co in Pd₃Co (Figure 1b).^[35]



Figure 2. HRTEM image of (a) Pd_3Co NCs (b) PdCo NCs and (c) Pd NPs at 5 nm scale. Inset: corresponding SAED pattern.



Figure 3. (a) TEM image of Pd_3Co NCs at 20 nm (b) Histogram showing average diameter of Pd_3Co NCs (c) HRTEM showing d-spacing (d) HAADF-STEM image of Pd_3Co NCs along with the EDS elemental maps of Pd (blue color) and Co shell (yellow color) and (e) EDX peaks of Pd_3Co NCs.

The morphology and structure of the nanocomposites were determined by transmission electron microscopy (TEM). HRTEM images of Pd₃Co, and PdCo NCs, and of Pd NPs are included as Figures 2a-2c, respectively. In all three cases, the spherical shape of the particles is evident. Furthermore, Pd₃Co NCs have spherical shapes (Figure 3a) with diameters ranging from 12 to 18 nm, with an average size of approximately 14.8 nm (Figure 3b). In addition, the HRTEM images clearly depict the lattice fringes of palladium and cobalt. The lattice fringe with a measured spacing of 0.22 nm corresponds to the (111) atomic plane of Pd, whereas the lattice fringe of the (101) plane (d = 0.19 nm) can be attributed to Co (Figure 3c). The high-angle annular dark-field scanning TEM (HAADF-STEM) elemental map reveals a homogeneous distribution of Pd (blue color) and Co (yellow color). This indicates the spatial arrangement of bimetallic Pd₃Co NCs (Figure 3d). Likewise, the energydispersive X-ray spectroscopy (EDS) coupled with TEM displayed characteristic peaks for Pd, Co, and O, as well as Cu and C due to the carbon-coated copper grid, which agrees with the compositional data from XPS (Figure 3e).

The initial weight loss (1.53 %) below 200 °C can be attributed to the loss of volatile material and adsorbed moisture on the Pd₃Co NCs, whereas the abrupt weight loss (20.38 %) after 200 °C may be due to the removal of the residual ethylene glycol adhered to the surface of the NCs.

Catalytic activity of Pd₃Co NCs

In order to demonstrate the applications and catalytic activity of the Pd_3Co NCs, Heck, Sonogashira, and Suzuki coupling reactions of iodonium ylides were carried out as model reactions. For these reactions, a variety of cyclic six-membered iodonium ylides **1a–1m** (Chart 1) was prepared (see the SI).





To optimize the reaction conditions, we investigated the coupling of 5,5-dimethyl-2-(phenyl- λ^3 - iodanylidene)cyclohexane-1,3dione (1a) and ethyl acrylate (2a) via the α -iodoenone intermediate (3a'), using different catalysts, solvents, and bases (Table 1). First, commercially available catalysts were screened. After refluxing 1a in toluene for 20 min, under inert conditions, 2a was added, followed by the addition of 2 mol% Pd(OAc)₂ and 2.0 equiv. of TEA, which afforded 3a, 3a', 3a'', and 3a''' in 15, 10, 59, and 12%, respectively, after 4 h (entry 1). Meanwhile, using 2 mol% Pd/C furnished 50, 30, 10, and 15% yields, respectively, (entry 2). Interestingly, the unexpected side product 3a''' was generated by the involvement of reaction of only phenyl group moiety on ylide 1a with 2a in low yield. With monometallic Pd

and Co NPs, compounds 3a, 3a', and 3a'' were obtained in 42, 30, and 10%, and 30, 51, and 7% yields, respectively (entries 3 and 4). Interestingly, the use of bimetallic PdCo NCs (2 mol%) afforded 3a in increased yield (80%), together with 3a' (9%) and 3a" (4%) (entry 5). This may be attributed to the coordination between Pd and Co atoms in the PdCo NCs that allows the high mobility of the electrons to vacant 5s, 5d and 5f-orbitals of Pd, partially filled 3d, and vacant 4p, 4d and 4f orbitals of Cobalt atom. The best yield of 3a (92%) was obtained using Pd₃Co NCs (2 mol%) and 2.0 equiv. of TEA (entry 6) due to the synergistic effect of Pd with Co metal in the Pd₃Co NCs. However, lowering the catalyst loading to 1 mol% and temperature to 80 °C did not improve the yield of desired product 3a. These results indicated the importance of the amount of catalyst loading and optimum temperature (entries 7-8). When TEA was replaced with inorganic bases K₂CO₃ and Cs₂CO₃. 3a was not isolated; instead 3a' was produced in 72-75% yields together with 3a" in 15-25% vields (entries 9 and 10). In the absence of TEA, only 3a' was isolated, in 85% yield (entry 11). Changing the solvent to DMF under reflux conditions afforded 3a (81%), and 3a" (15%) (entry 12). However, refluxing in THF did not produce 3a, affording instead 3a' and 3a'' in 80 and 5% yields, respectively (entry 13). Less coordinating solvents such as DMF and toluene are preferable for the formation of desired product 3a. Likewise, coordinating solvent THF provides stabilization to the intermediate 3a' which prevents further formation of product 3a.[36] Furthermore, performing the reaction as a one-pot procedure afforded, not only the desired product 3a but also 3a" in 65 and 20% yields, respectively (entry 14).

To explore the generality of the Heck-type coupling reaction, further reactions of different iodonium ylides and various acrylates were examined under the optimized conditions (Table 2). For example, the reaction of 5,5-dimethyl-2-(phenyl- λ^3 -iodanylidene)cyclohexane-1,3-dione (1a) with methyl acrylate (2b), t-butyl acrylate (2c), or phenyl acrylate (2d) afforded the desired products 3b-3d in 89-91% yields. Similarly, treatment of iodonium ylides 1b or 1e, bearing no substituent or phenyl group on the cyclohexanedione ring, with 2a, produced 3e and 3f in 89 and 96% yields, respectively. In addition, the reaction of 7-(phenyl- λ^3 -iodanylidene)spiro[3.5]nonane-6,8-dione (**1h**) bearing cyclobutyl group on the cyclohexanedione ring with ethyl acrylate (2a) gave the desired product 3f in 72% yield. Combination of 3-(phenyl- λ^3 -iodanylidene)chromane-2,4-dione (1k) with ethyl acrylate (2a), phenyl acrylate (2d), or phenyl methacrylate (2e) afforded compounds 3h-3j in 92-97% yields, 1-methyl-3-(phenyl-λ³-iodanylidene)quinolineand that of 2,4(1H,3H)-dione (1I) with 2b produced 3k in 78% yield. Reaction of 2-(phenyl- λ^3 -iodanylidene)-1*H*-phenalene-1,3(2*H*)dione (1m) with 2a successfully produced 3I in 96% yield. Moreover. treatment of 5,5-dimethyl-2-(p-tolyl-λ³iodanylidene)cyclohexane-1,3-dione (1g) bearing 4-Me group on the benzene ring with 2a provided the desired product 3m (78%).





^a Reaction conditions: **1a** (0.25 mmol) in toluene (3 mL) was refluxed for 20 min under N₂ atmosphere, followed by the addition of **2a** (0.75 mmol). Then, catalyst and base (2.0 equiv.) were added. ^b Isolated yields. ^c**1a** (0.25 mmol), **2a** (0.75 mmol), catalyst (2 mol%), and TEA (2.0 equiv.) were refluxed in toluene (3 mL) for 4 h under N₂ atmosphere.



^aReaction conditions: **1** (0.25 mmol) in toluene (3 mL) was refluxed for 20 min under N₂ atmosphere, followed by the addition of **2** (0.75 mmol). Then, Pd₃Co NCs (2 mol%) and TEA (2.0 equiv.) were added and refluxed for 4h. ^{*b*}Isolated yields.

Having proved the generality of this protocol in C-C bond forming reaction, we investigated the possibility of Sonogashira type coupling reactions of iodonium ylides (1a, or 1d–1f, or 1j-1m) with phenylacetylene (4a) and arylacetylenes 4b–4d (Table 3). Combination of iodonium ylides 1a, 1d, 1e, 1f, or 1j, bearing various substituents on the cyclohexanedione ring, with 4a, successfully produced the desired products 5a–5e in 80–90% yields. Treatment of 3-(phenyl- λ^3 -iodanylidene)chromane-2,4dione (1k) with phenylacetylene (4a), 4-ethynyltoluene (4b), or 1-ethynyl-4-fluorobenzene (4c) afforded products 5f–5h in 95, 91, and 90% yields, respectively, whereas that with 2ethynylthiophene (4d) produced 5i in 85% yield. Combination of 1-methyl-3-(phenyl- λ^3 -iodanylidene)quinoline-2,4(1*H*,3*H*)-dione (1I) with 4a afforded 5j in 90% yield, and that of 1m with 2a produced 5k in 86% yield. combined with **1a**, products **7d** and **7e** were isolated in 91 and 79% yields, respectively. Further combination of **1b-1c**, **1e**, **1g**-**1i**, or **1k-1m**, with **6a** or **6b** afforded **7f-7n** in 75–97% yields.

To illustrate the mechanism of these coupling reactions, control experiments were conducted on 5,5-dimethyl-2-(phenyl- λ^3 -iodanylidene)cyclohexane-1,3-dione, **1a** (Scheme 3). When **1a** was refluxed in toluene for 20 min, 2-iodo-3-phenoxycyclohex-2-en-1-one (**3a'**) was isolated in 90% yield (Scheme 3, eq. a). Further reaction of **3a'** with **2a**, under the optimized reaction conditions, afforded **3a** in 93% yield (Scheme 3, eq. b). These results suggest that **3a'** is the intermediate, and that the coupling reaction proceeds via the generation of α -iodoenone.



^aReaction conditions: **1** (0.25 mmol) in toluene (3 mL) was refluxed for 20 min under N₂ atmosphere, followed by the addition of **4** (0.375 mmol). Then, Pd₃Co NCs (2 mol%) and TEA (2.0 equiv.) were added and refluxed for 4h. ^bIsolated yields.

To investigate the versatility of the catalyst, Suzuki-type coupling reactions were next attempted with arylboronic acids (Table 4). In contrast with the results of the Heck and Sonogashira-type coupling reactions, treatment of 1a with phenylboronic acid (6a), under the optimized reaction conditions, using TEA as base, produced lower yield of the product 7a (40%). However, when TEA was replaced with 2 equiv. of K₂CO₃, 7a was produced in high yield (93%). For reactions of 1a with 4methoxyphenylboronic acid (6b) and 4-fluorophenylboronic acid (6c), bearing electron-donating and withdrawing groups, the desired products 7b and 7c were isolated in 91 and 80% yields, respectively. As observed for other arylboronic acids, when 2naphthylboronic acid (6d) and 2-thienylboronic acid (6e), were



^aReaction conditions: **1** (0.25 mmol) in toluene (3 mL) was refluxed for 20 min under N₂ atmosphere, followed by the addition of **6** (0.3 mmol). Then, Pd₃Co NCs (2 mol%) and K₂CO₃ (2.0 equiv.) were added and refluxed for 4h. ^bIsolated yields.

On the basis of this control experiment, and the literature concerning Heck, Sonogashira, and Suzuki coupling reactions, a plausible mechanism for the coupling of iodonium ylides **1a** with **2a**, **4a**, or **6a** is depicted in Scheme 4. For the Heck coupling cycle, first, when refluxed, iodonium ylide **1a** produces stable intermediate **3a'** through 1,3-phenyl migration. ^[37] Then, the Pd₃Co NCs undergo oxidative addition to **3a'** to form complex **8**. The coordination of olefin **2a** with **8** produces π -complex **9**, which undergoes olefin insertion, followed by β -H elimination, to afford **11**. Then, the active catalyst is regenerated through

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reductive elimination with the basic triethylamine, and **3a** is isolated. In Sonogashira coupling, the intermediate **8** reacts with phenylacetylene (**4a**) to produce complex **12**. The terminal alkyne of complex **12** is deprotonated to yield **13**, which affords final product **5a** and regenerates the active catalyst through reductive elimination. In the same way, for Suzuki coupling, in the presence of K_2CO_3 , complex **8** yields the intermediate **14**, which reacts with the boronate complex **15**, formed by in-situ reaction of boronic acid and K_2CO_3 , to form complex **16** via transmetallation. Reductive elimination liberates the active nanocatalyst and affords final product **7a**.



Scheme 3. Control experiments.



Scheme 4. Mechanistic pathway for the multivariate C-C coupling of iodonium ylides.

Recyclability and reusability test

One of the important properties of the prepared Pd₃Co nanocatalyst is its recoverability and reusability. The catalyst was recycled and reused five times. The recyclability test was 5,5-dimethyl-2-(phenyl-λ³carried using out iodanylidene)cyclohexane-1,3-dione (1a) in 1 mmol scale with corresponding amount of 2a for the Heck coupling reaction. In each cycle, after the completion of the reaction, the mixture was decanted. The mother liquor was transferred into a conical flask and the catalyst was recovered by centrifugation and subsequently washed with ethanol and dried in a hot air oven, prior to use for another catalytic cycle. The ethanolic wash was concentrated and added to the mother liquor for yield determination by column chromatography. However, after the fifth cycle, there was a slight decrease in the yield, which may be due to blocking of the active sites of the nanocomposites during the coupling reaction (Figure S2, see the SI). The nanocatalyst displayed high catalytic efficiency without any morphology and structural changes, which was confirmed by the respective TEM (Figure S3a, see the SI) and XRD analyses (Figure S3b, see SI).

Conclusions

Support-free Pd₃Co nanostructured composites were prepared via a hydrothermal approach, using readily available ethylene glycol as a mild reducing agent. The structural and catalytic properties of the nanostructured composites were investigated. XPS studies revealed that the elemental composition of the nanocomposites was 75% palladium and 25% cobalt. The Pd₃Co nanostructured composite exhibited enhanced selectivity with highest yield of coupled products. Moreover, the catalytic performance of support-free Pd₃Co has an edge over its monometallic counterparts and bimetallic PdCo catalyst particularly in view of Heck, Sonogashira, and Suzuki-type coupling reactions of iodonium ylides. Pd₃Co NCs has higher percentage of Pd indicating an enhanced amount of Pd in the catalyst can induce effective synergistic effect with Co metal thereby enhancing the overall catalytic efficiency. The coupling reaction hence becomes highly atom economy, which proceeds via the generation of α -iodoenones along with simultaneous migration of the phenyl group.

Experimental Section

Materials and Methods

All chemicals were commercially available and used as received, without further purification. Palladium(II) acetate, cobalt(II) acetate tetrahydrate, iodobenzene, ethyl acrylate, phenyl boronic acid, phenylacetylene, potassium carbonate, triethylamine, and toluene were obtained from Sigma-Aldrich.

Synthesis of support-free bimetallic Pd₃Co NCs

Pd₃Co NCs were prepared using one pot hydrothermal method with palladium(II) acetate (Pd(OAc)₂) and cobalt(II) acetate tetrahydrate (Co(OAc)₂·4H₂O) as the metal precursors, and ethylene glycol as the reducing agent. The calculated molar ratios of the precursor salts were added to a conical flask containing deionized water. The resulting mixture was sonicated for approximately an hour and transferred into a Teflon cup with a 50 mL inner volume. The autoclave was sealed carefully and heated to 120 °C, for 5 h, in a hot air oven. After completion of the hydrothermal process, the reaction mixture was allowed to cool at room temperature, and the resulting suspension was centrifuged at 12,000 rpm for 15 min. The residue was washed several times with DI water and ethanol, and dried in a hot air oven, under vacuum. The dried material was collected in a storage vial for further use. A similar synthetic procedure was adapted for the preparation of Pd NPs, Co NPs and PdCo NCs, with the use of 12 mg of Co(OAc)₂·4H₂O for the latter case.

Characterization of support-free bimetallic Pd₃Co NCs

X-ray diffraction (XRD) was performed on powdered samples on a PANalytical X'Pert PRO MPD (operating at 40 kV and 30 mA, with Cu Kα as the X-ray source ($\lambda = 1.5406$ Å) over the 2 θ angle range of 20° to 90°, and a scan rate of 1.2°/min). The elemental composition of the nanoparticles and the chemical state of each element were analyzed by X-ray photoelectron spectroscopy (XPS) using a Thermo Scientific, K-Alpha system fitted with an Al K α X-ray light source. The ion source energy ranged from 100 eV to 3 KeV for the survey. The size of the nanoparticles was determined by field emission transmission electron microscopy (FE-TEM, FEI Tecnai F20). The samples were prepared by placing a drop of the nanoparticle solution on a carbon-coated copper grid and allowing the solvent to evaporate in air at ambient temperature. The elemental make-up of the bimetallic nanoparticles was analyzed by high-angle annular dark-field scanning TEM energy-dispersive X-ray spectroscopy (HAADF-STEM-EDS) at 200 kV with a point resolution of 0.24 nm, a Cs and Cc of 1.2 mm each, and a focal length of 1.7 mm, using a Genesis liquid nitrogen cooled EDS detector with an ultrathin window. The thermal properties of the nanoparticles were analyzed by thermogravimetric analysis coupled with differential scanning calorimetry (DSC-TGA SDT-Q600 V20.5 Build 15) by heating under a N2 atmosphere to 1000 °C at a heating rate of 10 °C min⁻¹.

General procedure for the Heck coupling between iodonium ylides and acrylates

2-(Phenyl- λ^3 -iodanylidene)cyclohexane-1,3-dione (1a-1b, 1e, 1g–1h, 1j-1m) (0.25 mmol) and toluene (3 mL) were added to a round bottom flask equipped with a magnetic stirrer and reflux condenser. The mixture was refluxed in an oil bath for 20 min, under nitrogen atmosphere, then Pd₃Co nanocatalyst (2 mol%), acrylate (2a–2e) (2.5 equiv.), and TEA (2 equiv.) were added. After completion of the reaction, determined by TLC, the solvent was removed and the residue was purified by column chromatography on silica gel using hexane:ethyl acetate = 19: 1 as the solvent system, to afford the desired product. The structures of the products were assigned by spectroscopic analysis (see SI).

General procedure for the Sonogashira coupling between iodonium ylides and arylalkynes

2-(Phenyl- λ^3 -iodanylidene)cyclohexane-1,3-dione (1a, 1d-1f, 1j-1m) (0.25 mmol) and toluene (3 mL) were added to a round bottom flask equipped with a magnetic stirrer and reflux condenser. The mixture was refluxed in an oil bath for 20 min under nitrogen atmosphere, then the

 Pd_3Co nanocatalyst (2 mol%), arylalkynes (**4a–4d**), (1.2 equiv.), and TEA (2.0 equiv.) were added. After completion of the reaction, determined by TLC, the solvent was removed and the residue was purified by column chromatography on silica gel using hexane:ethyl acetate = 19: 1 as the solvent system, to afford the desired product. The structures of the products were assigned by spectroscopic analysis (see SI).

General procedure for the Suzuki coupling between iodonium ylides and boronic acids

2-(Phenyl- λ^3 -iodanylidene)cyclohexane-1,3-dione (1a–1c, 1e, 1g–1i, 1k-1m) (0.25 mmol) and toluene (3 mL) were added to a round bottom flask equipped with a magnetic stirrer and reflux condenser. The mixture was refluxed in an oil bath for 20 min under nitrogen atmosphere, then the Pd₃Co nanocatalyst (2 mol%), boronic acid (6a–6e) (1.2 equiv.), and K₂CO₃ (2.0 equiv.) were added. After completion of the reaction, determined by TLC, the solvent was removed and the residue was purified by column chromatography on silica gel using hexane:ethyl acetate = 19: 1 as the solvent system, to afford the desired product. The structures of the products were assigned by spectroscopic analysis (see SI).

Conflicts of interest

There are no conflicts to declare.

Acknowledgements ((optional))

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FULL PAPER

A green protocol for support-free and versatile Pd₃Co nanocomposites is designed using ethylene glycol. The synergistic effect of the nanocomposites further shows enhanced catalytic activity for the multivariate Heck, Sonogashira and Suzuki-type coupling reactions of iodonium ylides



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Support-free Pd₃Co NCs as an efficient heterogeneous nanocatalyst for novel organic transformations of C-C coupling reactions