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Organic Ligand Free Carbonylation Reactions with Unsupported **Bulk Pd as Catalyst**

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Here, surprising results are presented in bulk Pd catalyzed carbonylation reactions. Three types of carbonylation reactions can be realized efficiently under organic ligand-free conditions, i.e., hydroaminocarbonylation of olefins, aminocarbonylation of aryl iodides and oxidative carbonylation of amines, which almost covers all the known mechanisms in carbonylation reactions. Noteworthy, the bulk Pd catalyst system exhibited better catalytic activity than the classical homogeneous PdCl₂/(2-OMePh)₃P catalyst system. This study will create a momentous and new field in green carbonylation reactions.

In general, molecular catalysts have better catalytic activity and selectivity than heterogeneous catalysts. However, the difficulties in catalysts separation and recycling hinder their applications in industry. Heterogeneous catalysts are widely used in industry because it could be easily separated and recovered from reaction medium after reaction.^[1-2] For heterogeneous catalysts, the size of metal particles is one of the most important factors in determining the catalytic performance of the catalyst.^[3-5] Given that low-coordination, unsaturated atoms usually function as catalytically active sites and the catalytic activity of heterogeneous catalyst normally increased with the decreasing of the size of the metal particles. Recent results demonstrated that nano catalyst, subnano catalyst ^[5-19] and single atom catalyst ^[4, 10, 11] have better catalytic activity than bulk catalyst. In contrast, the potential of bulk metal as the catalyst may be tremendous and is worthy of investigation as the real structure of bulk metal catalyst may be composed by bulk particle body, and the self-supported nano-particles on the surface, as the surface of the bulk catalyst is usually crude. Therefore, the bulk metal particles might possess multi-metallic catalytic centers on the surface of the catalyst, in which the metal itself as support might exhibits unimaginable catalytic performance.

Carbonylation reaction is currently recognized as one of the most important industrial applications in the area of homogeneous catalysis

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and is emerging as especially useful and versatile tools for organic synthesis.^[23, 24] It is widely used for converting various chemicals into a diverse set of value-added and important carbonyl compounds, such as aldehydes, ketones, esters, amides and others, which have been widely applied in production of commodity chemicals, pharmaceuticals, and agrochemicals. However, the development of general and versatile heterogeneous catalyst for carbonylation reactions constitutes a significant challenge.

Based on the above discussions, we envisaged that bulk palladium self-supported nano-Pd would be useful for the establishment of general carbonylation reactions. Exactly, the first example of general and versatile organic ligand-free carbonylation reactions that include mainly three types of carbonylation reactions enabled by bulk palladium particle catalyst is realized (Scheme 1).



Initially, the palladium catalyst with different sizes including 148 nm 610 nm, and 1540 nm Pd powders (Alfa Aesar, item No. 043715, 000776, and 012068) were used in hydroaminocarbonylation reaction, [25-29] and the size of the palladium particles was determined by SEM images. The palladium catalysts are denoted as Pd-148, Pd-610, and Pd-1540, respectively. Following, the hydroaminocarbonylation reaction of styrene (1a) and aniline (2a) was used to optimize the reaction conditions with Pd-148 as catalyst, and the impact of different acidic additives including, Brønsted acids and Lewis acids on the reaction was investigated first (Table 1). Clearly, with the increase of acid strength of the acid additives, the conversion of aniline was improved, and a 91% conversion of aniline with 98% products selectivity was achieved when H₃PO₄ was used. However, the conversion of aniline was slightly decreased when the acid strength of the additives was further

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4a linear

increased. The reason might be attributed to the fact that the key palladium hydride species was difficult to form when the acid strength was too strong. Lewis acids such as Sc(OTf)₃ and Yb(OTf)₃•XH₂O have also been examined under the same condition, and no better results were obtained. These results showed that H₃PO₄ has a suitable acid strength for the formation of palladium hydride species which was considered to be a key reactive species in these processes for initiating the hydroaminocarbonylation.

h⁻¹ are obtained for Pd-610. Noteworthy, it has been found that the TOF numbers of Pd-610 are ~23 times higher than classical homogeneous PdCl₂/(2-OMePh)₃P and Pd(acac)₂/L catalyst systems. Even if don't take the dispersity into consideration, the homogeneous and heterogeneous system are similar. Therefore, the self-supported nano-Pd is indeed has a particular catalytic performance. This will give enlightenment for the application of bulk metal as a catalyst in catalytic transformations.

Table 2. The comparison of TON and TOF between homogeneous and heterogeneous carbonylation reaction of styrene with aniline.

3a branched

[Cat.] H₃PO₄ KI, 130°C, CO

1a

2a

$Ph \rightarrow Ph - NH_2 \xrightarrow{Cat} Ph + Ph \rightarrow Ph \xrightarrow{O} V'^{Ph}$										
	1a 2a		3 bran	a ched	4a linear					
Entry	Cat.	Acid	[1]	Conv. /% ^[b]	Sel./% [[] ^{b]}	b/l				
1	Pd-148	2-naphthol	KI							
2	Pd-148	B(OH) ₃	KI	4	>99	71:29				
3	Pd-148	HOAc	KI							
4	Pd-148	H ₃ PO ₄	KI	91	98	46:54				
5	Pd-148	TsOH	KI	30	92	40:60				
6	Pd-148	HCI	KI	84	97	51:49				
7	Pd-148	H_2SO_4	KI	59	89	28:72				
8	Pd-148	CF_3SO_3H	KI	44	90	54:46				
9	Pd-148	Sc(OTf) ₃	КІ	67	94	43:57				
10	Pd-148	Yb(OTf)₃- XH₂O	KI	16	41	54:46				
11	Pd-148		KI	trace						

^aReaction conditions: 1a (4.0 mmol), 2a (1.0 mmol), Pd-148 (1.0 mg), acid additive (5.0 mol%), KI (5.0 mol%), CO (40 bar), dioxane (2.0 mL), 130 °C, 12 h. ^bDetermined by GC-MS.

Furthermore, the catalytic performance of palladium with different sizes including Pd-148, Pd-610 and Pd-1540 were studied in details under the identical reaction conditions (Fig. 1 and Table S1). Clearly, 91% conversion of aniline with >99% selectivity was observed if Pd-148 was used as the catalyst. With the increasing of palladium sizes, the catalytic performance was slightly improved and 95% conversion of aniline with 98% selectivity (b/I = 35:65) was achieved when Pd-610 was employed as the catalyst. However, the conversion of aniline was decreased if the palladium size was further increased. The conversion was only 16% and selectivity was >99% if Pd-1540 was employed.

For comparison of the catalytic activities of palladium powder and homogeneous palladium catalysts, the TON (turnover numbers) and TOF (turnover frequencies) numbers were shown in Table 2. Firstly, the Pd dispersions of Pd-148, Pd-610 and Pd-1540 catalyst determined with H₂ titration technique are 6.6%, 3.9%, and 4.4%, respectively (Table 2). Based on the Pd dispersions of different bulk catalysts, the TON and TOF of Pd-148, Pd-610 and Pd-1540 are 1455, 2584, 388, and 121, 215, 32 h⁻¹, which are related to the active Pd species. It is clear that the catalytic activity of the bulk palladium is strongly dependent on the size of the bulk particles, and that the highest TON of 2584 and TOF of 215

Entry	Pd	dispersion (%)	Con. ^b	Based on all of Pd		Based on dispersion	
			(%)	TON	TOF(h ⁻¹)	TON	TOF(h ⁻
1	Pd-148	6.628	91	96	8.0	1455	121.3
2	Pd-610	3.897	95	101	8.4	2584	215.3
3	Pd-1580	4.372	16	17	1.4	388	32.3
4 ^c	Pd-610	3.897	11	58	4.9	1496	124.7
5 ^d	PdCl ₂ /(2- OMePh)P		95	19	9.5		
6 ^e	Pd(acac)₂ /L		99	198	9.9		

^aReaction conditions: 1a (4.0 mmol), 2a (1.0 mmol), Pd (1.0 mg), H₃PO₄ (5.0 mol%), KI (5.0 mol%), CO (40 bar), dioxane (2.0 mL), 130 °C, 12 h. ^bDetermined by GC-MS.^c 2a (5.0 mmol).^d reference 30.^e reference 27.

Subsequently, the effects of other parameters such as temperature, iodide compounds, solvent, pressure of the CO, amounts of H₃PO₄ and KI were also investigated. However, no improvement was observed (Table S2-7). Finally, the reducing of styrene to 2.0 equiv., had a negligible impact on the reaction (Table S2).

With the optimized conditions in hand, the scope of this bulk Pd catalyzed hydroaminocarbonylation reaction was investigated (Table 3). In general, both electro-donating and -withdrawing substituents on the benzene ring of aromatic amines were well-tolerated under the current conditions. Unfortunately, currently it is difficult to modulate the regioselectivity with this bulk Pd catalyst. With electron-rich methyl-, tertbutyl-, and methoxy-substituted anilines as starting materials, good to excellent yields (83-99%) with moderate regioselectivities (b/l = 56 : 44 - 71:29) were achieved (3a-3g, 4a-4g). Electron-deficient anilines bearing fluoro, chloro and ester groups also proceeded well, affording their corresponding products in 70-97% yields with moderate regioselectivities (b/l = 50 : 50 - 62 : 38) (3h-3j, 4h-4j). In addition, the reaction of 8-aminoquinoline, as an example of heterocyclic substrate, provided the corresponding product in 91% yield with moderate regioselectivity (b/l = 60:40) (3k, 4k). No conversion was observed when aliphatic amine, i.e., hexylamine, was employed as substrate, which might be ascribed to the competition of the amine with the alkene for surface sites of Pd. Next, reactions of aniline with different olefins were examined. It was noted that the electronic nature on the phenyl ring of the styrene had a strong influence on the reactivity and regioselectivity.

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In general, styrenes bearing an electro-withdrawing group on their aryl ring exhibited higher reactivity than electro-donating group. For example, the reaction of 4-bromostyrene with aniline provided the corresponding product in 99% yield while only 74% yield was obtained with 4-methylstyrene as starting material. It is noteworthy that the bromo group could survive the reaction conditions, which is useful handles for further synthetic elaborations with transition metal catalysis. Furthermore, we turned our attention to more challenging aliphatic alkenes. Gratifyingly, allylbenzene and terminal aliphatic alkenes with long chains furnished the desired hydroaminocarbonylation products in excellent yields with ratio of b/l from 50 : 50 to 42 : 58 (3p-3s, 4p-4s). We suppose that the I/b ratio should be decided by several factors, such as the electrophilicity of amine and the steric hindrance of Pd-COalkene intermediate. The I/b ratio would be close to 50 : 50 if the electrophilicity of amine is weak, i.e., o-F-aniline, or the steric hindrance of Pd-CO-alkene intermediate is lower. In reverse, the more linear products would be obtained.



^aReaction conditions: alkenes (2.0 mmol), amines (1.0 mmol), Pd-610 (1 mg), KI (5 mol%), H₃PO₄ (5 mol%), CO (40 bar), dioxane (2.0 mL), 130 $^{\circ}$ C, 24 h. ^bYield of isolated. ^cRegioselectivity was determined by yield of isolated. ^dPd-610 (4 mg), KI (5 mol%), H₃PO₄ (20 mol%).

To demonstrate the potential synthetic utility of this protocol, we performed the reaction on a gram scale and desired products were obtained in 82% NMR yields, thus demonstrating the scalability of this reaction (Scheme 2). Importantly, the catalyst could be reused in the hydroaminocarbonylation of styrene with aniline for at least 3 times without deactivation.



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In order to test if the active species are palladium leached from the bulk phase during the reaction, a control reaction was performed. The reaction mixture was filtered after reacted for 3 h and the filtrate was allowed to react for another 9 h. Indeed, we found that reaction stopped without further progressing (Fig. 1). Therefore, the selfsupported nano-Pd is the real catalyst and no catalytically active palladium species is dissolved in the solution. Moreover, the Hg poisoning experiment was performed in order to provide further evidence of the nature of the catalytic system (homogeneous vs. heterogeneous). First, the reaction mixture was detected after reacted for 3 h and the conversion of aniline was 12%. Then, 550 mg Hg metal (275 equiv.) was added into the reaction mixtures and allowed to react for another 9 h, and the final conversion of aniline was 11%. As control reaction, the Hg poisoning experiment of homogeneous Pd catalyst was performed following the typical operation in ref. 30. First, A mixture of styrene (11.0 mmol), aniline (1 mmol), PdCl₂ (5 mol% based on aniline), P(2-OMePh)₃ (0.12 mmol) and THF 10 mL were added a glass tube which was placed in an 100 mL autoclave. Then the autoclave was purged and charged with CO (50 atm). The reaction mixture was stirred at 125 °C. Then the reaction mixture was detected after being reacted for 1 h and the conversion of aniline was 45%. Then, 550 mg Hg metal was added into the reaction mixtures and allowed to further react for another 1 h, and the final conversion of aniline was 76%. So the Hg poisoning experiment clearly proved that large excess of Hg didn't affect the activity of the homogeneous palladium catalyst system and the heterogeneous nature of the Pd power catalyst in this work can be confirmed. [31]



It is well known that transition metal-catalvzed aminocarbonylations of C-X bonds with amines is an important strategy for the synthesis of amides which represent a ubiquitous functional group in pharmaceutically relevant compounds.^[32-35] Given the robustness of above aminocarbonylations of alkenes with amines, we investigated the aminocarbonylation of aryl iodides and amines with the bulk Pd catalyst by slightly changing the reaction conditions (Table S8-S10). At first, aminocarbonvlation reactions of iodobenzene with amines were studied. A variety of amines, including aliphatic primary amines, aromatic primary amines, cyclic secondary amines, and acyclic secondary amines are all readily converted into the desired amides in 88-99% yields (Table 4, 7a-7e). Importantly, the catalyst could be reused for the aminocarbonylation reactions of iodobenzene with aniline at least three catalytic cycles with keeping its good catalytic performance (7a). Furthermore, we investigated the scope of aryl iodides. In generally, both electron-donating and electron-withdrawing Green Chemistry gins

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groups in aryl iodides were all compatible with these aminocarbonylation conditions, affording the desired products in 81-99% yields (**7f-7j**). Substituent at the ortho position slightly decreased the product yield, which might arise from steric hindrance (**7h**). As expected, naphthalene substrate also underwent this transformation smoothly, giving the desired product in excellent yield (**7k**).

Table 4. Bulk Pd-catalyzed aminocarbonylation of aryl iodides and amines.^a



^aReaction conditions: amines (1.5 mmol), aryl iodides (1.0 mmol), Pd-610 (1 mg), K₂HPO₄ (2.0 mmol), CO (5 bar), dioxane (2.0 mL), 130 $^{\circ}$ C, 12 h. ^bYield of isolated. ^cCatalyst was recovered and reused at the third run.

As it is known, the oxidative carbonylation of amines is considered as an important strategy for synthesis of the symmetric ureas^[36-39], which are useful intermediates for the production of pharmaceuticals, agricultural chemicals and phosgene-free synthesis of isocynates. The robustness of above aminocarbonylations of alkenes and aryl iodides has promoted us to further investigate the possibility of using bulk Pd as catalyst to realize the oxidative carbonylation of the amines. As shown in Table 5, oxidative carbonylation of aliphatic primary amines such as n-hexylamine, n-heptanamine and benzylamine proceeded well, providing the corresponding products in excellent yields (9a-9c). In addition, bulky substituted cyclohexylamine also underwent this transformation smoothly to afford the desired product in 99% yield (9d). Moreover, aromatic primary amines were converted into the corresponding products in excellent yields (9e-9i). Furthermore, cyclic secondary amine also reacted smoothly to give the corresponding urea in 94% yield (9j).



 a Reaction conditions: amines (2.0 mmol), Pd-610 (1 mg), CO (35 bar), O_2 (5 bar), dioxane (2.0 mL), 130 $^\circ\!\!C$, 24 h. Yield of isolated.

Based on the above discussions, it can be seen that the bulk Pd exactly possess superior activity in the carbonylation reactions. However, we still need to verify the structure of the bulk Pd. Therefore,

these palladium particles were characterized by XPS, XRD, SEM and TEM. Initially, XPS characterization was employed to investigate the variations of binding energy of fresh and used three times bulk Pd-610 catalysts (Fig. S2 and Table S10). The Pd 3d_{5/2} peak at 335.4 eV is attributed to Pd(0) (metallic palladium). According to XPS data, metallic palladium was mainly formed on the surface of the fresh catalyst, and PdO was also observed, as the surface palladium is easy to be oxidized in air The XPS spectra of catalyst sample Pd-610 used three times did not detect palladium peaks and the content of surface oxygen species of the used catalyst is much higher than fresh catalyst (Fig. S2). This observation should be reasonable, because oxidative addition of H₃PO₄ to Pd(0) gives the palladium hydride species which have higher content of surface oxygenic species after water washing than bulk palladium. In addition, the palladium particle surface was covered by carbon materials, which might be formed via the polymerization of olefin. However, the formation of carbon layer on the catalyst surface does not influence it activity. Next, the Pd-610 catalyst before and after being used for 3 times were characterized by XRD (Fig. S3 and Table S11). From the analysis of the XRD patterns, the fresh Pd-610 catalyst shows diffraction peaks at 40.1°, 46.7°, 68.1°, 82.1° and 86.7°, which can be ascribed to the diffraction peaks of Pd (111), Pd (200), Pd (220), Pd (311), and Pd (222). Besides above Pd diffraction peaks, a new diffraction peak at 18.1° was observed after Pd-610 catalyst being used for three times. However, the attribution of this peak is still not determined. It can not be attributed to the diffraction patterns of KI, PdI₂, KH₂PO₄ and K₂HPO₄. Meanwhile, some small diffraction peaks can be observed at 29.3° and 31.5°, which might belong to K_2HPO_4 and K₂HPO₄ in situ generated from KI and H₃PO₄ during the reaction.



Fig. 2 SEM images of catalysts. (a) Pd-148, (c) Pd-610, (e) Pd-1540. TEM images of catalyst. (b) Pd-148, (d) fresh Pd-610. (f) Pd-1540, (g) Pd-610 used one time, (h) Pd-610 used three times.

Furthermore, SEM and TEM were used to reveal the microstructure of the Pd-148, Pd-1540, fresh and used bulk Pd-610 catalyst. SEM image (Fig. 2a, 2c, 2e) showed that the size of the different bulk palladium particles is about 148 nm, 610 nm, and 1540 nm, which is confirmed by the TEM image in Fig. S1. TEM image (Fig. 2b) showed that the Pd-148 particles are formed by accumulation of smaller-sized Pd particles. According to the TEM images shown in Fig. 2d, the fresh catalyst Pd-610 is composed by bulk particle body, and the nano-Pd layer are selfsupported on the surface of the bulk Pd catalyst. The catalyst sample

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used one to three times was further characterized by TEM. As can be seen from Fig. 2g and 6h the body of bulk Pd still is bulk particles and the nano-Pd particles are evidently self-supported on the bulk Pd surface after being used.

Conclusions

In summary, we have successfully developed the general and versatile carbonylation reactions using a bulk Pd catalyst under organic ligand free conditions. By applying an acid additive, aminocarbonylation of wide range of olefins with amines are efficiently transformed into the corresponding amides in good to excellent yields. Moreover, the aminocarbonylation of aryl iodides with amines could also be established when K₂HPO₄ was addition to the reaction. In addition, the oxidative carbonylation of a variety of amines for symmetric urea synthesis could also be realized by this catalyst. Such general and versatile catalytic activation may be attributed to the formation of multi-metallic active sites with multidimensional cooperative activation function of the self-supported nano-Pd on the bulk palladium surface. The study should be provided useful inspiration to apply bulk catalysts in catalysis and synthetic chemistry.

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Notes and references

- P. Munnik, P. E. de Jongh, K. P. de Jong, Chem. Rev. 2015, 115, 6687-6718.
- G. A. Somorjai, J. Y. Park, Angew. Chem. Int. Ed. 2008, 47, 9212-9228; Angew. Chem. 2008.
- J. P. den Breejen, P. B. Radstake, G. L. Bezemer, J. H. Bitter, V. Froseth, A. Holmen, J. Am. Chem. Soc. 2009, 131, 7197-7203.
- X. F. Yang, A. Wang, B. Qiao, J. Li, J. Liu, T. Zhang, Acc. Chem. Res. 2013, 46, 1740-1748.
- K. Yamamoto, T. Imaoka, W. J. Chun, O. Enoki, H. Katoh, M. Takenaga, *Nat. Chem.* 2009, 1, 397-402.
- S. Vajda, M. J. Pellin, J. P. Greeley, C. L. Marshall, L. A. Curtiss, G. A. Ballentine, *Nat. Mater.* 2009, 8, 213-216.
- Y. Lei, F. Mehmood, S. Lee, J. Greeley, B. Lee, S. Seifert, *Science* 2010, 328, 224-228.
- L. Liu, U. Diaz, R. Arenal, G. Agostini, P. Concepcion, A. Corma, Nat. Mater. 2017, 16, 132-138.
- S. Zhang, C. R. Chang, Z. Q. Huang, J. Li, Z. Wu, Y. Ma, J. Am. Chem. Soc. 2016, 138, 2629-2637.
- B. Qiao, A. Wang, X. Yang, L.F. Allard, Z. Jiang, Y. Cui, Nat. Chem. 2011, 3, 634-641.
- R. Lang, T. Li, D. Matsumura, S. Miao, Y. Ren, Y. T. Cui, Angew. Chem. Int. Ed. 2016, 55, 16054-16058; Angew. Chem. 2016, 128, 16288-16292.
- M. E. Broussard, B. Juma, S. G. Train, W. J. Peng, S. A. Laneman, G. G. Stanley, *Science* 1993, **260**,1784-1788.
- 13. C. Li, E. Widjaja, M. Garland, J. Am. Chem. Soc. 2003, 125, 5540-5548.
- R. C. Matthews, D. K. Howell, W. J. Peng, S. G. Train, W. D. Treleaven, G. G. Stanley, Angew. Chem. Int. Ed. 1996, 35, 2253-2256.
- 15. G. Sussfink, Angew. Chem. Int. Ed. 1994, 33, 67-69.
- 16. Z. Chen, M. Furutachi, Y. Kato, S. Matsunaga, M. Shibasaki, Int. Ed.

2009, 48, 2218-2220; Angew. Chem. 2009, 121, 2252-2254.

- 17. S. Jautze, R. Peters, Angew. Chem. Int. Ed. 2008, **47**, 9284-9288; Angew. Chem. 2008, **47**, 9284-9288.
- Z. Zhang, Z. Wang, R. Zhang, K. Ding, Angew. Chem. Int. Ed. 2010, 49, 6746-6750; Angew. Chem. 2010, 122, 6898-6902.
- Y. Nishibayashi, M. Yamanashi, II. Wakiji, M. Hidai, Angew. Chem. Int. Ed. 2000, 39, 2909-2911; Angew. Chem. 2000, 112, 3031-3033.
- B. Kosog, C. E. Kefalidis, F. W. Heinemann, L. Maron, K. Meyer, J. Am. Chem. Soc. 2012, 134, 12792-12797.
- D. C. Powers, M. A. Geibel, J. E. Klein, T. Ritter, J. Am. Chem. Soc. 2009, 131, 17050-17051.
- Y. Y. Zhou, C. Uyeda, Angew. Chem. Int. Ed. 2016, 55, 3171-3175; Angew. Chem. 2016, 128, 3223-3227.
- 23. M. Beller, Catalytic carbonylation reactions, Springer, 2010.
- 24. L. Kollár, Modern carbonylation methods, Wiley-VCH, 2008.
- Y. Tsuji, T. Ohsumi, T. Kondo, Y. Watanabe, J. Organomet. Chem. 1986, 309, 333-344.
- 26. B. ElAli, K.Okuro, G. Vasapollo, H. Alper, J. Am. Chem. Soc. 1996,118, 4264-4270.
- X. Fang, R. Jackstell, M. Beller, Angew. Chem. Int. Ed. 2013, 52, 14089-14093; Angew. Chem. 2013, 125, 14339-14343.
- 28. S. I. Lee, S.Son, Y. K. Chung, Chem. Commun. 2002, 1310-1311.
- G. Zhang, B. Gao, H. Huang Angew. Chem. Int. Ed. 2015, 26, 7657-7661; Angew. Chem. 2015, 127, 7767-7771.
- 30. H. Liu, N. Yan, P. J. Dyson, Chem. Commun. 2014, 50, 7848-7851.
- N. T. S. Phan, M. Van Der Sluys, C. W. Jones, Adv. Synth. Catal. 2006, 348, 609 - 679.
- F. Ozawa, H. Soyma, T. Yamamoto, *Tetrahedron Lett.* 1982, 23, 3383-3386.
- 33. T. Kobayashi, M. Tanaka, J. Organomet. Chem. 1982, 233, 64-66.
- Y. Uozumi, T. Arii, T. Watanabe, J. Organomet. Chem. 2001, 66, 5272-5274.
- 35. T. T. Dang, Y. Zhu, S. C. Ghosh, Chem. Commun. 2012, 48,1805-1807.
- R. A. Franz, F. Applegath, F. V. Morriss, J. Organomet. Chem. 1961, 26, 3309-3312.
- N. Sonoda, T. Yasuhara, K. Kondo, J. Am. Chem. Soc. 1971, 93, 6344-6344.
- F. Shi, Y.. Deng, T. SiMa, . Angew. Chem. Int. Ed. 2003, 42, 3257-3260; Angew. Chem.2003, 115, 3379-3382.
- 39. Ca. N. Della, P. Bottarelli, A. Dibenedetto, J. Catal. 2011, 282, 120-127.

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Unsupported bulk Pd catalyzed carbonylation reactions have been developed for the first time under organic ligand free condition without the addition of organic ligand.