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Phosphine-Free, Efficient Double Carbonylation of Aryl Iodides with Amines Catalyzed by Water-Insoluble and Water-Soluble N-Heterocyclic Carbene–Amine Palladium Complexes

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Abstract: The water-insoluble and water-soluble N-heterocyclic carbene (NHC)–amine palladium complexes, Ipr-Pd(deba)Cl and SO₃-Ipr-Pd(deba)Cl, were synthesized. Both catalysts exhibit excellent activity in the phosphine-free double carbonylation of aryl iodides with amines to produce α -keto amides. Moreover, as the water-soluble catalyst exhibits significant compatibility in the aqueous phase with the activities of different Pd-NHC complexes, we con-

clude that the intramolecular amine ligand strongly affects the selectivity of the products in double carbonylation reaction and serves as an alternative of phosphine ligands.

Keywords: double carbonylation; N-heterocyclic carbene-amine palladium complexes; phosphine-free reaction; water-soluble complexes

Introduction

The α -keto amides are versatile intermediates in the organic synthesis of a variety of useful products including α -keto acids, α -hydroxy acids and heterocyclic compounds.^[1] As a consequence, the development of synthetic methods to produce α -keto amides has attracted considerable attention. Among all the synthetic routes, transition metal-catalyzed double carbonylation of aryl halides with nucleophiles has been widely used.^[2] Since its discovery by Ozawa,^[3] the palladium-catalyzed double carbonylation of aryl halides has been extensively studied to produce α -keto amides. Various palladium phosphine catalyst systems have been reported to promote the transformation of aryl halides to α -keto amides, and all the reported catalysts contain phosphine ligands such as PPh₃,^[4] PPh₂Me, PCy₃,^[5] or PBu₃.^[2e] The most efficient catalytic system was reported by Uozumi and co-workers using Pd/PPh₃ in the presence of triethylenediamine (DABCO) as a base to provide excellent yields of the α -keto amides.^[6] However, the preparation of these phosphine ligands and their derivatives typically in-

volves substances of poor air-stability and they are, in general, expensive, which limits their application. Hence, the development of a low-cost phosphine-free catalyst which could efficiently catalyze the double carbonylation reaction is the subject of the present work. Recently, Castillón and co-workers^[7] reported the first Pd-catalyzed phosphine-free double carbonylation system with [Pd(η^3 -C₃H₅)(μ -Cl)]₂/DBU (DBU = 1,3-diazabicyclo[5.4.0]undecane) to produce α -keto amides with excellent selectivity, and proposed that DBU acts as a ligand, a nucleophile and a base at the same time. However, a more efficient and economic phosphine-free Pd-catalyzed system is needed for double carbonylation.

N-heterocyclic carbenes (NHCs) were also used in various organic reactions as ligands due to their strong donor ability and stability of the resulting metal complexes.^[8] This makes NHCs available for maintaining efficient activity in carbonylation because the reaction is always carried out under rigorous conditions. Up to now, Pd-NHC complexes have been successfully applied for some carbonylation reactions.^[9] Ryu^[10] and co-workers employed a Pd-NHC-

PPh_3 complex in the double carbonylation of aryl iodides with amines in $[\text{BMIm}]\text{PF}_6$ in a microreactor. However, the PPh_3 ligand also was indispensable.

There is also growing interest in using NHCs as a basis for new ligand platforms that display unusual reactivity. Several hybrid ligand sets based on NHC have been prepared including those of N-donors. Through N-donors, a large range of steric and electronic effects can be imparted on the metal center.^[11] Amine functionalized NHC-metal complexes have shown high activity in C–C coupling reactions,^[12] and hydrogenation.^[13] By combining the NHC with the N-donor amine, herein, we have developed the first NHC–amine–Pd system without the use of phosphine in the double carbonylation of aryl iodides with amines.

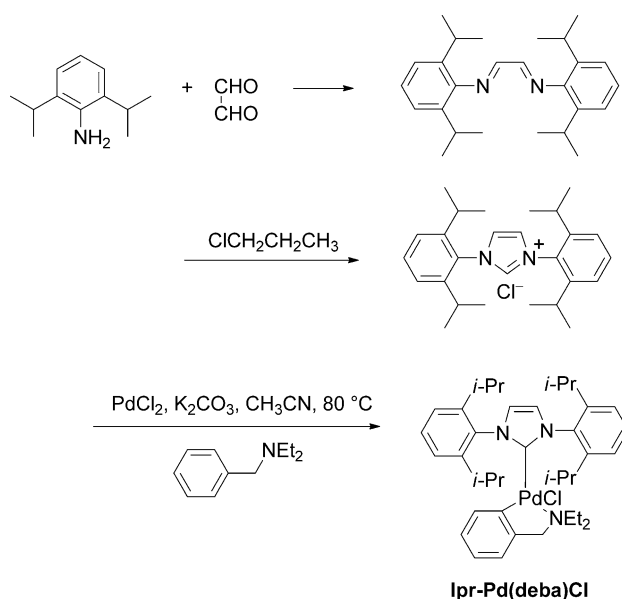
Ipr $[N,N'-(2,6\text{-diisopropylphenyl})\text{dihydroimidazol-2-ylidene}]$ represents the state-of-the-art in bulky ligands, as demonstrated by their widespread use in homogeneous catalysis. efficient synthesis on a large scale, the ease of handling the imidazolium precursor and unique ability to stabilize reactive transition metal intermediates.^[14] Simultaneously, palladium precatalysts with bulky NHC ligands have established themselves as successful alternatives to palladium–phosphine complexes in Pd-catalyzed C–C cross-coupling reactions.^[15] Herein, we report the Pd-catalyzed double carbonylation of aryl iodides with amines using the Ipr NHC as the active ligand.

In a related context, water-soluble catalysts constitute also an attractive choice. Water especially as a cheap and non-toxic solvent has been receiving special attention. Water-soluble complex catalysts combine the advantages of homogeneous and heterogeneous catalysis: simple and complete separation of the product from the catalyst, high activity, and high selectivity.^[16] Among all the water-soluble complexes bearing chelating NHC ligands, sulfonated NHC-based metal complexes have appeared to be an interesting type of catalyst that can provide improved catalytic properties.^[17] For the aim to achieve the reuse of the catalysts, a sulfonated NHC–amine Pd catalyst was prepared and studied in the aqueous double carbonylation reactions.

Thus, continuing our works on phosphine-free carbonylation reactions,^[18] we herein report phosphine-free water-insoluble and water-soluble NHC–amine palladium complexes catalysts for the double carbonylation of aryl iodides with amines. The mechanism of double carbonylation catalyzed by NHC–amine palladium complexes is discussed.

Results and Discussion

Ipr-Pd(deba)Cl was synthesized as previously reported^[19] with PdCl_2 and N,N -diethylbenzylamine (deba)



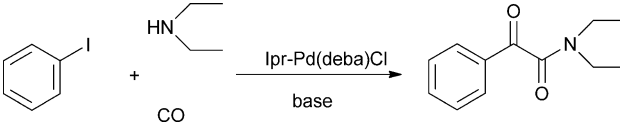
Scheme 1. The synthesis of the Ipr-Pd(deba)Cl complex.

in HPLC-grade acetonitrile in air in the presence of an excess of K_2CO_3 . Then the prepared NHC precursor Ipr·HCl was added leading to an 85% yield of NHC–amine palladium complex Ipr-Pd(deba)Cl (Scheme 1).

The catalytic performance of the NHC–amine Pd complex in double carbonylation reactions of aryl iodides with amines was studied. The reaction between iodobenzene and diethylamine was chosen as the benchmark reaction for initial investigations with a CO pressure of 2.0 MPa over the catalyst with a palladium loading of 0.5 mol%. The influence of various reaction parameters, including solvent, base and reaction time, on the reaction were investigated, and the results are summarized in Table 1. Among the used solvents including 1,4-dioxane, CH_3CN , THF and toluene, 1,4-dioxane produced the highest yield of 86%. Among the organic and inorganic bases studied, K_2CO_3 was proved to be the best. It is also observed that decreasing the reaction time from 12 h to 8 h leads to the yield of α -keto amide being reduced from 86% to 76%. Therefore, the carbonylation reaction was optimized and performed with Ipr-Pd(deba)Cl (0.5 mol%), 1,4-dioxane and K_2CO_3 at 80 °C under 2.0 MPa of CO for 12 h.

Under the optimized conditions, the substrates of the double carbonylation reaction were explored using substituted iodobenzene and different amines. As shown in Table 2, the double carbonylation reaction of diethylamine with a variety of aryl iodides proceeded smoothly, producing the corresponding double carbonylation products **3a–3e** in moderate to high yields. Various electron-donating and electron-withdrawing groups, such as CH_3 , OCH_3 , Cl, Br, on the

Table 1. Effects of bases and solvents on the double carbonylation of iodobenzene with diethylamine catalyzed by Ipr-Pd(deba)Cl.^[a]



Entry	Solvent	Base	Time [h]	Yield [%] ^[b]
1	1,4-dioxane	K ₂ CO ₃	12	86
2	CH ₃ CN	K ₂ CO ₃	12	74
3	THF	K ₂ CO ₃	12	47
4	PhCH ₃	K ₂ CO ₃	12	53
5	1,4-dioxane	KO- <i>t</i> -Bu	12	36
6	1,4-dioxane	K ₃ PO ₄	12	30
7	1,4-dioxane	Cs ₂ CO ₃	12	78
8	1,4-dioxane	Et ₃ N	12	44
9	1,4-dioxane	pyridine	12	28
10	1,4-dioxane	K ₂ CO ₃	8	76

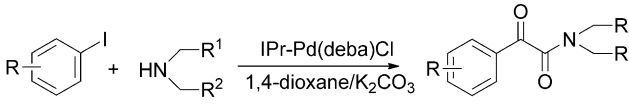
^[a] Reaction conditions: iodobenzene (1.0 mmol), diethylamine (5.0 mmol), Ipr-Pd(deba)Cl (0.5 mol%), solvent (5.0 mL), base (2.0 mmol), CO (2.0 MPa), 80 °C.

^[b] Isolated yield.

aryl iodide were well sustained (Table 2, entries 1–5). The double carbonylation reactions of morpholine were also carried out with aryl iodides under mild conditions. Various electron-donating and electron-withdrawing groups, such as CH₃, OCH₃, NO₂, Cl, Br, on the aryl iodide were well sustained to give the desired α -keto amides in good to high yields (Table 2, entries 6–14). The double carbonylation reactions of primary amines such as propylamine and aniline gave corresponding α -keto amides **3o** and **3p** in 83% and 89% yields, respectively (Table 2, entries 15 and 16). Bromobenzene showed no activity in the double carbonylation system.

The aforementioned experimental results demonstrated that the phosphine-free catalyst Ipr-Pd(deba)Cl showed high activity in the double carbonylation reaction. However, the complex is difficult to be recycled for further use. Enhanced environmental consciousness promoted the efficiency of chemical reactions under benign conditions with recycling and reuse of the catalysts, a trait that has become an integral part of chemical research today.^[20] So, our studies were continued further for the synthesis of a recyclable NHC–amine palladium complex and its application in the double carbonylation reaction. A number of approaches have been developed to recycle homogeneous catalysts. The predominant one is to anchor the catalyst onto various kinds of supports, such as silica-based materials,^[21] magnetic nanoparticles^[22] and polymers,^[23] by which the catalyst can be recycled from the reaction mixture by simple filtration and separation. Another one is to develop a biphasic reac-

Table 2. Double carbonylation of aryl iodide with amine catalyzed by Ipr-Pd(deba)Cl.^[a]



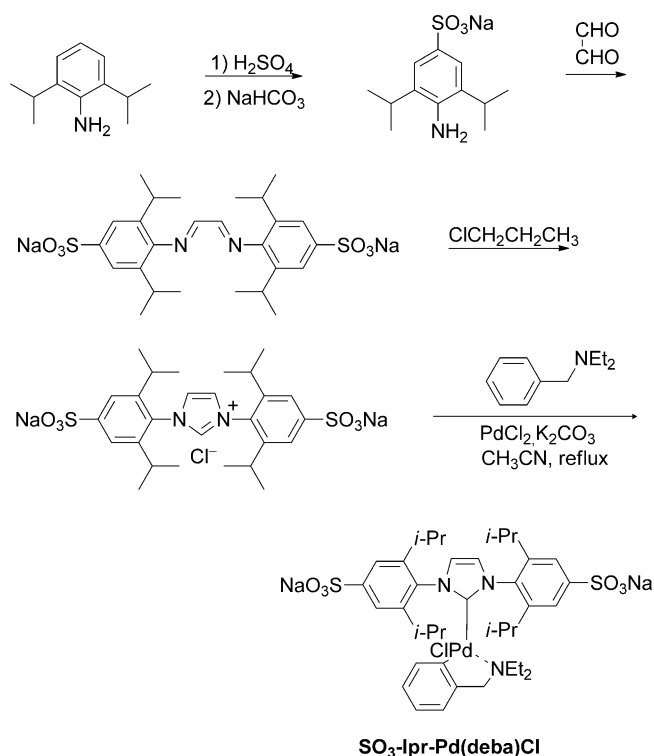
Entry	Aryl iodide	Amine	Product	Yield ^[b] /Selec. ^[c] [%]
1		HNEt ₂	3a	86/98
2		HNEt ₂	3b	56/64
3		HNEt ₂	3c	82
4		HNEt ₂	3d	86/93
5		HNEt ₂	3e	89
6			3f	92/98
7			3g	47/57
8			3h	84
9			3i	86
10			3j	89
11			3k	86
12			3l	67/76
13			3m	60/72
14			3n	84/91
15			3o	83
16			3p	89
17		HNEt ₂	—	—

^[a] Reaction conditions: aryl iodide (1.0 mmol), amine (5.0 mmol), 1,4-dioxane (5.0 mL), Ipr-Pd(deba)Cl (0.5 mol%), K₂CO₃ (2.0 mmol), CO (2.0 MPa), 80 °C, 12 h.

^[b] Isolated yield.

^[c] Determined by GC-MS.

tion system wherein the catalyst and the reaction mixture dissolve in different phases, such as the aqueous biphasic system. The design of catalysts containing li-



Scheme 2. The synthesis of the sulfonated NHC-amine palladium complex SO₃-Ipr-Pd(deba)Cl.

gands with hydrophilic substituents has been the most common approach to constrain a catalyst to the aqueous part of a biphasic reaction mixture.^[24]

With the success of the NHC-amine palladium complex as an efficient phosphine-free double carbonylation catalyst, we proceeded further to prepare a water-soluble NHC-amine palladium complex catalyst. Among the various water-soluble ligands, the sulfonate group is the most prominent solubilizing group.^[25] Shaughnessy and co-workers^[26] described the first remarkable example using water-soluble imidazolium inner salts with covalently bonded sulfonate anions as ligand precursors to synthesize Ag(I) and Pd(II) NHC complexes. Inspired by this, we prepared the disulfonated N-heterocyclic carbene palladium complex SO₃-Ipr-Pd(deba)Cl. As shown in Scheme 2, the preparation started from the sulfonated 2,6-diisopropylaniline,^[25] and then followed the synthesis process for Ipr-Pd(deba)Cl.

In order to evaluate the catalytic performance of SO₃-Ipr-Pd(deba)Cl for double carbonylation reactions in aqueous media, we studied the double carbonylation of iodobenzene and diethylamine in water. Using different bases (NEt₃, K₃PO₄, K₂CO₃, KO-*t*-Bu) in the aqueous media, the results showed that KO-*t*-Bu has a significant influence on the catalytic activity (Table 3, entries 1–4). The catalyst system is amphiphatic. When water is used as the solvent with KO-*t*-Bu as the base, HO-*t*-Bu will exist in the aqueous

Table 3. Effects of bases and solvents on the SO₃-Ipr-Pd(deba)Cl-catalyzed double carbonylation of iodobenzene in water.^[a]

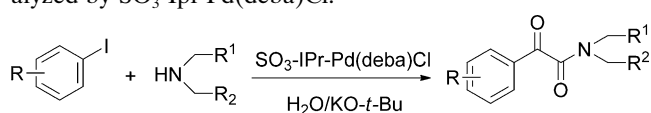
Entry	Base	Time [h]	Yield [%] ^[b]
1	NEt ₃	6	45
2	K ₃ PO ₄	6	70
3	K ₂ CO ₃	6	47
4	KO- <i>t</i> -Bu	6	76
5	KO- <i>t</i> -Bu	12	84

^[a] Reaction conditions: iodobenzene (1.0 mmol), diethylamine (5.0 mmol), H₂O (5.0 mL), SO₃-Ipr-Pd(deba)Cl (1.0 mol%), base (2.0 mmol), CO (2.0 MPa), 100 °C.

^[b] Isolated yield.

media due to hydrolysis of KO-*t*-Bu as detected by GC-MS. Thus the complex catalyst could be dissolved in HO-*t*-Bu, forming a homogeneous micro-environment system. Such a micro-homogeneous system could promote the yield of α-keto amides as a result. When the reaction time was increased to 12 h from 6 h, the yield of α-keto amides increased to 84% from 76% (Table 3, entries 4 and 5). Thus, the optimized conditions for this aqueous double carbonylation reaction with catalyst SO₃-Ipr-Pd(deba)Cl (1.0 mol%) are reaction at 100 °C using KO-*t*-Bu as the base at 2.0 MPa carbon monoxide for 12 h.

To examine the scope of this two-phase double carbonylation reaction, we have investigated the reactions using a variety of aryl iodides and amines as substrates under the optimized reaction conditions. The results are summarized in Table 4. The double carbonylation reactions of diethylamine with a variety of aryl iodides proceeded smoothly under mild conditions, producing the corresponding double carbonylation products in good-to-high yields (Table 4, entries 1–7). The double carbonylation reaction of aryl iodides with electron-donating substituents such as CH₃ and OCH₃ with diethylamine went smoothly, providing moderate to excellent product yields (Table 4, entries 2–4). As for aryl iodides substituted with electron-withdrawing groups such as Cl and Br, fairly high product yields were also achieved from their double carbonylation reactions with diethylamine, as seen from entries 5 and 6 in Table 4. The double carbonylation of bulky idonaphthalene with diethylamine provided the α-keto amide in 82% yield (Table 4, entry 7). Furthermore, we investigated the double carbonylation reaction of morpholine with a variety of aryl iodides under mild conditions. Various electron-donating and withdrawing groups, such as CH₃, OCH₃, Br, Cl and NO₂ on aryl iodides were

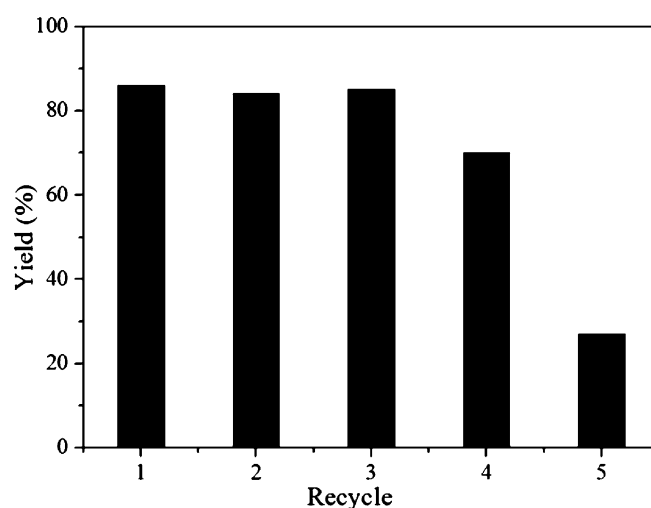
Table 4. Double carbonylation of aryl iodide with amine catalyzed by $\text{SO}_3\text{-Ipr-Pd(deba)Cl}$.^[a]

Entry	Aryl iodide	Amine	Product	Yield ^[b] [%]
1		HNEt_2	3a	84
2		HNEt_2	3b	47
3		HNEt_2	3q	73
4		HNEt_2	3c	76
5		HNEt_2	3d	77
6		HNEt_2	3e	89
7		HNEt_2	3r	82
8			3f	82
9			3g	27
10			3h	83
11			3i	89
12			3j	96
13			3t	78
14			3l	72
15			3m	75
16			3n	86
17			3u	92

^[a] Reaction conditions: aryl iodide (1.0 mmol), amine (5.0 mmol), H_2O (5.0 mL), $\text{SO}_3\text{-Ipr-Pd(deba)Cl}$ (1.0 mol%), KOt-Bu (2.0 mmol), CO (2.0 Mpa), 80°C , 12 h.

^[b] Isolated yield.

well sustained to give the desired α -keto amides in moderate to high yields (Table 4, entries 8–11, 13–17).

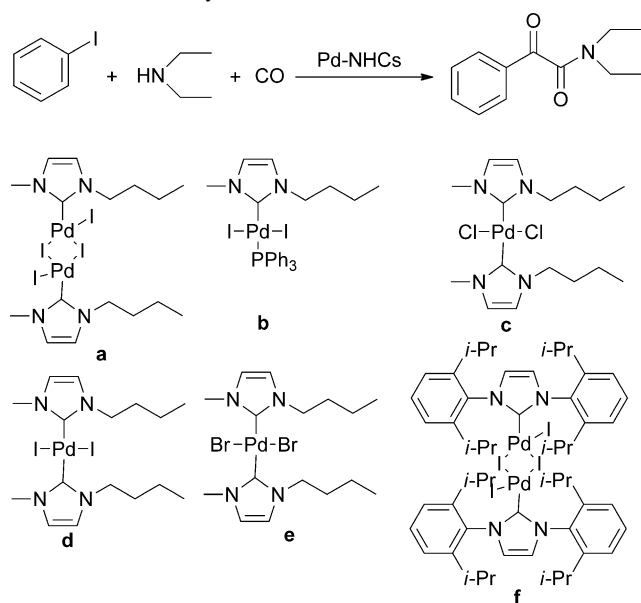
**Figure 1.** Catalyst reusability study. Reaction conditions: 4-nitroiodobenzene (1.0 mmol), morphine (5.0 mmol), CO (2.0 Mpa), $\text{SO}_3\text{-Ipr-Pd(deba)Cl}$ (1.0 mol%), H_2O (5.0 mL), KOtBu (2.0 mmol), 100°C , 12 h.

In addition, the double carbonylation of iodonaphthalene with diethylamine also provided the desired α -keto amide in 96% yield (Table 4, entry 12).

The prepared water-soluble NHC–amine palladium catalyst not only exhibited catalytic activities for the double carbonylation reaction in aqueous media, but also can be easily recovered by simple extraction. We further investigated the double carbonylation reaction of 4-nitroiodobenzene with morpholine in water with recycled catalyst, and the product yields are plotted against the catalyst recycling times (Figure 1). There was no significant decrease in product yield during the first three cycles; however, the yield decreased down to 70% for the fourth cycle, and to 27% for the fifth cycle. The reduction in yield was mainly due to the leaching of water-soluble palladium catalysts to the organic phase in the extraction process. Atomic absorption spectroscopic (AAS) analysis was used to assess the extent of Pd leaching. After the first cycle, 23% of initial Pd was detected in the organic phase. During the first cycle, the loading of the catalyst (1.0 mol%) was initially in excess for the reaction, thus the leaking of the water-soluble Pd complex catalyst to the organic phase did not influence the activity of the catalyst in the next two runs.

In order to identify functional groups of the NHC–amine palladium complex for the catalytic activity, some previously reported NHC–Pd complexes (as shown in Table 5)^[9b] were also investigated for the double carbonylation of iodobenzene with diethylamine. In general, no catalytic activity was observed for the catalyst **c** $(\text{BMIm})_2\text{PdCl}_2$. A yield of only 17% was achieved for the catalyst **e** $(\text{BMIm})_2\text{PdBr}_2$. Compared to both catalysts containing Cl and Br ions, the Pd complexes containing iodide anions $[(\text{BMIm})\text{PdI}]_2$

Table 5. Pd-NHCs used in the double carbonylation of iodobenzene with diethylamine.^[a]



Entry	1	2	3	4	5	6
Catalyst	a	b	c	d	e	f
Yield [%]	43	87	0	46	17	54

^[a] Reaction conditions: iodobenzene (1.0 mmol), diethylamine (5.0 mmol), 1,4-dioxane (5.0 mL), NHC-Pd complex (0.25 mol%), K₂CO₃ (2.0 mmol), CO (2.0 Mpa), 90 °C, 5 h.

a and (BMIm)₂PdI₂ **d** showed better catalytic activity, giving the product yields of 43% and 46%, respectively. The bulky ligand IPr-Pd complex **f** was also synthesized and investigated for the double carbonylation reaction with the product yield of 54% being obtained. All these results indicate that the complex catalysts with an NHC group generally produced low yields of α -keto amides, and the intramolecular amine ligand in IPr-Pd(deba)Cl strongly affects the selectivity of the double carbonylative reaction. The (BMIm)PdPPh₃ **b** exhibited considerably enhanced catalytical activity, which gave an 87% yield of the double carbonylation product under the same conditions. This indicated that the amine containing Pd-NHC complex exhibited comparable performance as the phosphine containing Pd-NHC complex, and the amine ligand played a similar role as phosphine in double carbonylation reactions.

Conclusions

In summary, we have developed two novel, phosphine-free catalysts for the double carbonylation reactions of aryl halides with amines by using the water-

insoluble catalyst IPr-Pd(deba)Cl in 1,4-dioxane and the water-soluble catalyst SO₃-IPr-Pd(deba)Cl in aqueous media. Both phosphine-free catalysts exhibited high activity towards the double carbonylation reaction for the production of α -keto amides. The reusability testing of SO₃-IPr-Pd(deba)Cl demonstrated high catalytic activity during the first three cycles. It is proposed that the excellent activities of Pd-NHC-amine catalysts would enable us to better understand phosphine-free catalysts for double carbonylation reactions.

Experimental Section

General Remarks

All chemicals were of reagent grade and used as purchased, unless otherwise mentioned. All solvents were purified according to standard procedures before use. The products were purified by flash chromatography on silica gel and identified by comparison of their spectra with those of standard samples. The ¹H and ¹³C NMR spectra were recorded on a Bruker Avance 400 MHz NMR spectrometer (400 and 100 MHz, respectively), chemical shifts are given in ppm with reference to tetramethylsilane (TMS) as internal standard. Elemental analyses were carried out on a Vario EL analyzer. GC-MS was performed on an Agilent 6890/5973 GC-MS, and ESI-MS on a Micro-QOF-II mass instrument.

Synthesis of IPr-Pd(dmmba)Cl

A three-necked flask (50 mL) was charged with PdCl₂ (177 mg, 1.0 mmol), CH₃CN (20 mL, HPLC grade) and *N,N*-diethylbenzylamine (209 mg, 1.05 mmol). The stirred mixture was heated at reflux until a clear, dark orange solution was formed and PdCl₂ had dissolved completely. Then powdered K₂CO₃ (345 mg, 2.5 mmol) was added and stirred until the solution changed to canary yellow. Afterward, IPr-HCl (445 mg, 1.05 mmol) was added in one portion and refluxed for another 30 min. After cooling down, the mixture was diluted with CH₂Cl₂, filtered, and dried under vacuum.

Synthesis of SO₃-IPr-Pd(deba)Cl

With a similar procedure as for IPr-Pd(dmmba)Cl, SO₃-IPr-Pd(deba)Cl was prepared as a yellow solid, using PdCl₂ (177 mg, 1.0 mmol), *N,N*-diethylbenzylamine (209 mg, 1.05 mmol), CH₃CN (20 mL, HPLC grade), K₂CO₃ (345 mg, 2.5 mmol) and SO₃IPr-HCl (612 mg, 1.05 mmol). SO₃IPr-HCl was synthesized starting from sodium 2,6-diisopropylaniline-4-sulfonate.

General Procedure for the Double Carbonylation Reaction

All double carbonylation reaction experiments were carried out in a 75-mL autoclave equipped with magnetic stirring and automatic temperature control. The autoclave reactor was charged with aryl iodide (1.0 mmol), amine (5.0 mmol), base (2.0 mmol), the catalyst and solvent (5.0 mL), and then

with carbon monoxide up to a pressure of 2.0 MPa. Afterward, the reactor was heated for several hours. After cooling down to room temperature, the reaction mixture was sampled for GC-MS analysis, and dried. The remaining solid was purified by chromatography on silica gel.

Recycling of the Catalyst

A 75-mL autoclave was charged with nitroiodobenzene (1.0 mmol), morpholine (5.0 mmol), $\text{SO}_3\text{-Ipr-Pd(deba)Cl}$ (1.0 mol%), H_2O (5.0 mL), $\text{KO-}t\text{-Bu}$ (2.0 mmol) and then pressurized with carbon monoxide at 2.0 MPa. The reactor was then heated at 100°C for 12 h. After cooling down to room temperature, the products were extracted by ethyl acetate. The aqueous phase was then transferred to a new reactor for the next cycle. Yields were determined by chromatography on silica gel.

Acknowledgements

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