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Double carbonylation of aryl iodides with diethylamine catalyzed by dinuclear palladium complexes

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Abstract

Dinuclear palladium complexes bridged by a novel PNNP ligand, *N,N′*-bis[(2-diphenylphosphino)phenylformamidinate (dpfam), were found to be very efficient and selective catalysts for the double carbonylation of iodobenzene with diethylamine using K_3PO_4 as base and 1,4-dioxane as solvent with a TON up to 10^5 and selectivity of 96%.

Keywords: Carbon monoxide; Double carbonylation; Aryl iodide; Dinuclear palladium complexes

1. Introduction

Palladium-catalyzed double carbonylation of aryl, alkenyl, and alkyl halides has been the subject of intensive study [1] since its discovery in 1982 by Ozawa, Yamamoto and co-workers [2] and by Kobayashi and Tanaka [3]. The reactions produce α-keto amides [4–6], esters [7,8], and acids [9] depending on the nucleophiles employed. They are versatile intermediates in organic synthesis for α-hydroxy acids [10,11], α-amino acids [12], and others [13]. The α-keto amides are formed with high selectivity by use of alkylphosphine [4] or bidentate phosphine like 1,4-bis(diphenylphosphino)butane (dppb) [3] as the ligand of palladium. We have synthesized a number of palladium and platinum bimetallic complexes bridged by a novel PNNP ligand, *N,N′*-bis[(2-diphenylphosphino)pheny]formamidinate (dpfam) in which the two metal atoms are forced into close proximity (Scheme 1). Treatment of Hdpfam with two equivalents of Pd(Me)Cl(tmeda) afforded the homobimetallic complex, Pd_2Me_2(μ-Cl)(μ-dpfam) (**1a**). Trichloro complex **1b** and iodo-bridged di(*p*-tolyl) complex **1c** were prepared similarly. The heterobimetallic complex, $PdPtMe_2$(μ-Cl)(μ-dpfam) (**2**) was obtained by the reaction of PtMeCl(cod) with PdMe(dpfam) (**4**), which was prepared from the reaction of Hdpfam with $PdMe_2$(tmeda). The platinum dinuclear complex Pt_2Me_2(μ-Cl)(μ-dpfam) (**3**) was synthesized by a method similar to that for dipalladium complex **1a** [14]. Two metal centers in close proximity may have the possibility to have a cooperative effect, both improving the efficiency and selectivity of catalyzing and promoting reactions that are not possible using a single metal center. Although the application of bimetallic complexes as catalysts seems to be limited [15–17], high efficiency of a dirhodium complex has been verified in the hydroformylation reaction of α-olefins [18]. Promoting effects of CuI as co-catalyst on the palladium-catalyzed double carbonylation reaction of iodobenzene have also been demonstrated in which an iodo-bridged palladium–copper species has been postulated as intermediate [19]. Here we report on the features of the dinuclear palladium complexes as catalyst in the double carbonylation of aryl halides with diethylamine.

2. Results and discussion

Usually double carbonylation of aryl halides with amines to give α-keto amides is conducted in the absence of solvent. We have examined several solvents and bases for the double carbonylation of iodobenzene, since adequate adjustment of the reaction parameters may

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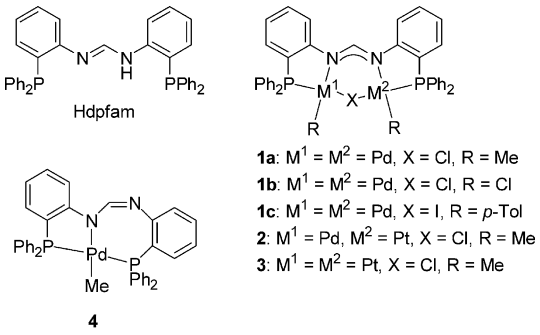


Scheme 1.

be necessary for use of dinuclear complexes as catalyst. Diethylamine was employed as the pertinent secondary amine in consideration of the previous studies for obtaining α-keto amides. Reaction of iodobenzene with 1.5 equivalents of diethylamine in the presence of base and 0.1 mol% of chloro-bridged dinuclear palladium complex **1a** under 20 atm of carbon monoxide at 100 °C for 15 h afforded a mixture of the single carbonylation product *N,N*-diethylbenzamide (**5**) and the double carbonylation product *N,N*-diethylphenylglyoxamide (**6**).

$$\mathrm{PhI + CO + Et_2NH \xrightarrow{Cat.\ 1a} \underset{5}{PhCONEt_2} + \underset{6}{PhCOCONEt_2}}$$

Representative results are summarized in Table 1. The carbonylation reaction using K_2CO_3 as base proceeded efficiently in a nonpolar solvent like benzene (entry 1) or toluene (entry 2) with fair selectivity for the double carbonylation product **6**. Similar results were obtained from the reaction using acetonitrile as solvent (entry 3). The reaction proceeded most selectively in 1,4-dioxane (entry 4). Dichloromethane was not a suitable solvent in terms of total yield and selectivity for **6** (entry 5). Polar aprotic solvents such as DMSO, DMF, and DMAc generally demonstrated poor selectivity for **6** (entries 6–8).

Table 1
Effect of solvent on double carbonylation of iodobenzene with diethylamine

Entry	Solvent	Total yield (%) [a]	**5/6**
1	Benzene	> 99	25/75
2	Toluene	> 99	27/73
3	CH_3CN	99	26/74
4	1,4-Dioxane	96	20/80
5	CH_2Cl_2	62	82/18
6	DMSO	85	58/42
7	DMF	> 99	53/47
8	DMAc	> 99	70/30

Reactions were carried out at 100 °C for 15 h in 5 ml of solvent under 20 atm of CO using 2.0 mmol of PhI, 3.0 mmol of Et_2NH, and 2.0 mmol of K_2CO_3 in the presence of 0.1 mol% of **1a**.

[a] GC yield.

The effects of bases on the double carbonylation of iodobenzene with diethylamine were examined using 1,4-dioxane as solvent and 0.1 mol% of the dinuclear palladium complex **1a** as catalyst. Results are summarized in Table 2. When diethylamine was used as base as well as substrate, poor selectivity for **6** was obtained (entry 1). Inorganic bases such as K_2CO_3, Cs_2CO_3, CsF, and K_3PO_4 exhibited good selectivity for **6** in general (entries 2–5). Among them, K_3PO_4 was exceptional (entry 5). Successful use of inorganic bases has been reported in the palladium-catalyzed double carbonylation of iodobenzene to give phenylglyoxylic acid [20]. Good results were obtained with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as base (entry 6). Organic bases such as ^{t}BuOK (entry 7), AcOK (entry 8), 1,4-diazabicyclo[2.2.2]octane (DABCO; entry 9), pyridine (entry 10), and *N,N*-dicyclohexylmethylamine (Cy_2NMe; entry 11) showed poor yield and moderate selectivity for **6**. Although DABCO has been reported to be a suitable base for double carbonylation of iodobenzene with *n*-butylamine in the presence of a palladium-triphenylphosphine complex [21], this is not the case for the present reaction.

To evaluate the efficiency of the dinuclear complex **1a** as catalyst on the double carbonylation of iodobenzene with diethylamine, effect of the loading of **1a** was studied with K_3PO_4 as base and 1,4-dioxane as solvent. Results are given in Table 3. The carbonylation reaction with high loading of 10% proceeded efficiently with very low selectivity of 19% (entry 1). The selectivity for **6** was improved considerably to 66% with 1% loading of **1a** (entry 2). The tendency to improve the selectivity for **6** was also observed in lower loading regions. Thus, the selectivity could be increased up to 84, 84, 87, and 96% without significant decrease in the total yield when the loading of **1a** was reduced to 0.5, 0.25, 0.1, and 0.01%

Table 2
Effect of base on double carbonylation of iodobenzene with diethylamine

Entry	Base	Total yield (%) [a]	**5/6**
1	Et_2NH [b]	> 99	65/35
2	K_2CO_3	96	20/80
3	Cs_2CO_3	89	28/72
4	KF	86	31/79
5	K_3PO_4	> 99	13/87
6	DBU	99	19/81
7	^{t}BuOK	31	68/32
8	AcOK	31	65/35
9	DABCO	45	49/51
10	Pyridine	24	58/42
11	Cy_2NMe	38	45/55

Reactions were carried out at 100 °C for 15 h in 5 ml of 1,4-dioxane under 20 atm of CO using 2.0 mmol of PhI, 3.0 mmol of Et_2NH, 2.0 mmol of base in the presence of 0.1 mol% of **1a**.

[a] GC yield.

[b] Total 8.0 mmol of Et_2NH was used as substrate and base.

Table 3
Effect of loading of **1a** on double carbonylation of iodobenzene with diethylamine

Entry	**1a** (mol%)	Concentration of **1a** (M)	Et_2NH/PhI (molar ratio)	Et_2NH/1a (molar ratio)	Concentration of Et_2NH (M)	Total yield (%) [a]	**5/6**
1 [b]	10	67×10^{-4}	1.5	15	0.1	97	81/19
2 [c]	1	33×10^{-4}	1.5	150	0.5	92	34/66
3 [c]	0.5	17×10^{-4}	1.5	300	0.5	90	16/84
4 [c]	0.25	8×10^{-4}	1.5	600	0.5	91	16/84
5 [d]	0.10	7×10^{-4}	1.0	1000	0.7	57	18/82
6 [e]	0.10	7×10^{-4}	1.5	1500	1.0	99	13/87
7 [f]	0.10	7×10^{-4}	15.0	15,000	10.0	97	9/91
8 [g]	0.01	1.7×10^{-4}	1.5	15,000	2.5	81	4/96
9 [g]	0.001	0.17×10^{-4}	1.5	150,000	2.5	51	4/96
10 [g,h]	0.001	0.17×10^{-4}	1.5	150,000	2.5	98	4/96

Reactions were carried out at 100 °C for 15 h in 3 ml of 1,4-dioxane under 20 atm of CO in the presence of **1a**.
[a] GC yield.
[b] 0.2 mmol of PhI, 0.3 mmol of Et_2NH, 0.2 mmol of K_3PO_4.
[c] 1.0 mmol of PhI, 1.5 mmol of Et_2NH, 1.0 mmol of K_3PO_4.
[d] 2.0 mmol of PhI, 2.0 mmol of Et_2NH, 2.0 mmol of K_3PO_4.
[e] 2.0 mmol of PhI, 3.0 mmol of Et_2NH, 2.0 mmol of K_3PO_4.
[f] 2.0 mmol of PhI, 30 mmol of Et_2NH, 2.0 mmol of K_3PO_4.
[g] 5.0 mmol of PhI, 7.5 mmol of Et_2NH, 5.0 mmol of K_3PO_4.
[h] Forty-eight hours.

with a fixed diethylamine/iodobenzene ratio of 1.5 (entries 3, 4, 6, 8). Even 0.001% loading of **1a** exerted catalysis to afford **6** with 96% selectivity. In this case, however, the total yield declined to 51% (entry 9). The yield reached 98% with a turnover number (TON) as high as 10^5 after a reaction time of 48 h (entry 10). When 1.0 equivalent of diethylamine was employed, the selectivity for **6** declined to 82% with moderate total yield of 57% (entry 5). The selectivity was improved to 91% with excellent total yield of 97% when large excess of diethylamine (15 equivalents) was used (entry 7). It is apparent that the amount of diethylamine employed affects both total yield and selectivity. The improvement in selectivity may be associated with the increase in concentration of diethylamine or the increase in diethylamine/**1a** ratio. To clarify the effect of the concentration of diethylamine on the reaction, experiments were performed with a fixed diethylamine/**1a** ratio of 15,000. The results are given in Table 4. Initially, the effects of carbon monoxide pressure were studied, since the reactions were performed under 10 atm of carbon monoxide different from that used in Table 3. Both the selectivity and the yield were effected little in the range of 10–30 atm (entries 1–3). Concentration was varied by changing the amount of solvent. The selectivities were almost unchanged in the concentration of diethylamine 1.5–7.5 M region (entries 3–6). Taking the results in Table 3 and those in Table 4 into consideration, the improvement in selectivity was most likely associated with the increase in diethylamine/**1a** ratio.

Diethylamine was used so far as the pertinent amine for the double carbonylation based on the studies conducted with mononuclear catalysts. Other amines

Table 4
Effect of concentration of diethylamine on double carbonylation of iodobenzene in the presence of **1a**

Entry	Concentration of diethylamine (M)	CO (atm)	Total yield [a] (%)	**5/6**
1 [b]	1.5	30	79	3/97
2 [b]	1.5	20	81	4/96
3 [b]	1.5	10	76	4/96
4 [c]	2.5	10	88	3/97
5 [d]	3.8	10	79	4/96
6 [e]	7.5	10	78	5/95

Reactions were carried out at 100 °C for 15 h in 1,4-dioxane using 5.0 mmol of PhI, 7.5 mmol of Et_2NH, and 5.0 mmol of K_3PO_4 in the presence of 0.01 mol% of **1a**.
[a] GC yield.
[b] Five milliliters of 1,4-dioxane.
[c] Three milliliters of 1,4-dioxane.
[d] Two milliliters of 1,4-dioxane.
[e] One milliliter of 1,4-dioxane.

may have some different influence on the yield and selectivity in the reactions using binuclear complex **1a** as catalyst. Table 5 shows the effect of various amines on the carbonylation of iodobenzene in the presence of 0.01% of dinuclear complex **1a**. Secondary amines of high basicity ($pK_b \leq 4$) were suitable for reaction (entries 1 and 2). On the other hand, the steric bulkiness of amine has a great influence on the yield of α-keto amides. Diisopropylamine seems too bulky to undergo double carbonylation (entry 3) whereas less sterically demanding amines such as pyrrolidine (entry 4) and piperidine (entry 5) showed high reactivity with moderate selectivity. Primary amines are reported to undergo

Table 5
Double carbonylation of iodobenzene with various amines

Entry	Amine (pK_b)	Total yield (%) [a]	Amide/keto amide
1	Et_2NH (3.00)	88[b]	3/97
2	$^nPr_2NH$ (3.00)	75	7/93
3	$^iPr_2NH$ (2.95)	31	100/0
4	Pyrrolidine (2.87)	91	51/49
5	Piperidine (2.80)	96	32/68
6	$^nBuNH_2$ (3.32)	95	21/79
7	$PhNH_2$ (9.34)	68	100/0
8	PhNHMe (9.15)	33	100/0
9	PhNHEt (9.38)	31	100/0
10	$PhCH_2NHMe$ (4.15)	79	33/67

Reactions were carried out at 100 °C for 15 h in 3 ml of 1,4-dioxane under 10 atm of CO using 5.0 mmol of PhI, 7.5 mmol of amine, and 5.0 mmol of K_3PO_4 in the presence of 0.01 mol% of **1a**.
[a] Isolated yield.
[b] GC yield.

the secondary reaction with α-keto amide formed to afford Schiff bases exclusively [3,4b]. In our reactions, *n*-butylamine gave α-keto amide in 79% selectivity and 95% total yield with negligible formation of the Schiff base (entry 6). This may be ascribed to the smaller amounts of amine used (1.5 equivalents) than that used in the reaction reported previously where the amine was used as solvent. Less basic amines such as aniline, *N*-methylaniline, and *N*-ethylaniline did not afford the double carbonylation products (entries 7–9). *N*-benzylmethylamine had moderate selectivity for the formation of α-keto amide (entry 10). The trends obtained here were similar in principle with those obtained under mononuclear catalysis.

Table 6 summarizes the results obtained with various aryl iodides. Introduction of an electron-donating group such as MeO (entry 1) or Me (entry 2) at the para position of iodobenzene resulted in a decrease in reactivity and an increase in selectivity for the α-keto amide. On the contrary, introduction of an electron-withdrawing group such as Cl (entry 4) or NO_2 (entry 5) increased the reactivity and decreased the selectivity. This tendency is similar to that demonstrated under mononuclear catalysis reported previously [4b]. The 1-iodonaphthalene was a poor substrate for this double carbonylation (entry 6) which might be attributed to the steric hindrance caused by the peri-hydrogen. The 2-iodonaphthalene readily underwent double carbonylation with fair selectivity of 81%. All the 2-iodoheteroarenes tested demonstrated similar trends in terms of selectivity. Thus, 2-iodopyridine, 2-iodofuran, and 2-iodothiophene had poor selectivity for the double carbonylation product showing the effects exerted by the adjacent heteroatom (entries 9–11). The 3-iodopyridine and 3-iodothiophene gave moderate selectivity for the α-keto amide (entries 8 and 12). An efficient double carbonylation of 4-iodopyridine to produce the corresponding pyridylglyoxylic acid derivatives has been reported with a $Pd(dba)(PCy_3)_2$ catalyst [6].

Table 6
Double carbonylation of various aryl iodides with diethylamine

Entry	Aryl iodide	Total yield (%) [a]	Amide/keto amide
1	*p*-$MeOC_6H_4I$	69	4/96
2	*p*-MeC_6H_4I	70	3/97
3	C_6H_5I	88[b]	3/97
4	*p*-ClC_6H_4I	95	11/89
5	*p*-$O_2NC_6H_4I$	87	76/24
6	1-Iodonaphthalene	11	36/64
7	2-Iodonaphthalene	73	19/81
8	3-Iodopyridine	78	44/56
9	2-Iodopyridine	45	96/4
10	2-Iodofuran	25	100/0
11	2-Iodothiophene	91	98/2
12	3-Iodothiophene	89	38/62

Reactions were carried out at 100 °C for 15 h in 3 ml of 1,4-dioxane under 10 atm of CO using 5.0 mmol of aryl iodide, 7.5 mmol of Et_2NH, and 5.0 mmol of K_3PO_4 in the presence of 0.01 mol% of **1a**.
[a] Isolated yield.
[b] GC yield.

The influence of several homo- and hetero-binuclear palladium complexes as well as mononuclear palladium complexes on the double carbonylation reaction was studied using iodobenzene and 1.5 equivalents of diethylamine at 0.01 mol% complex loading (Table 7). All the dinuclear palladium complexes such as chloro-bridged dimethyl complex **1a**, trichloro complex **1b**, and iodo-bridged di(*p*-tolyl) complex **1c** exhibited good

Table 7
Effect of several binuclear and mononuclear complexes on double carbonylation of iodobenzene with diethylamine

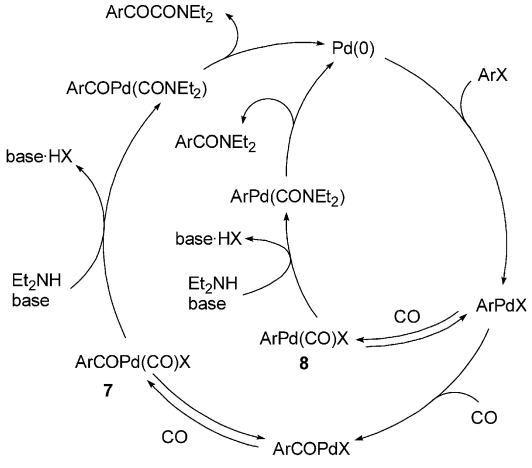
Entry	Complex	Total yield (%) [a]	**5/6**
1	**1a**	88	3/97
2	**1b**	65	6/94
3	**1c**	69	9/91
4	**2**	77	5/95
5	**3**	0	-
6	**4**	74	3/97
7 [b]	**1a**	93	28/72
8 [b]	**4**	71	37/63
9	$PdCl_2(PPh_3)_2$	68	26/74
10	$PdCl_2$(dppe)	72	15/85
11	$PdCl_2$(dppp)	78	6/94
12	$PdCl_2$(dppb)	57	5/95
13	$PdCl_2$(dppf)	76	30/70

Reactions were carried out at 100 °C for 15 h in 3 ml of 1,4-dioxane under 10 atm of CO using 5.0 mmol of PhI, 7.5 mmol of Et_2NH, and 5.0 mmol of K_3PO_4 in the presence of 0.01 mol% of complex.dppe = 1,2-bis(dipenylphosphino)ethane; dppp = 1,3-bis(dipenylphosphino)propane; dppb = 1,4-bis(dipenylphosphino)butane; dppf = 1,1′-bis(diphenylphosphino)ferrocene.
[a] GC yield.
[b] 1.0 mol% of complex was employed.

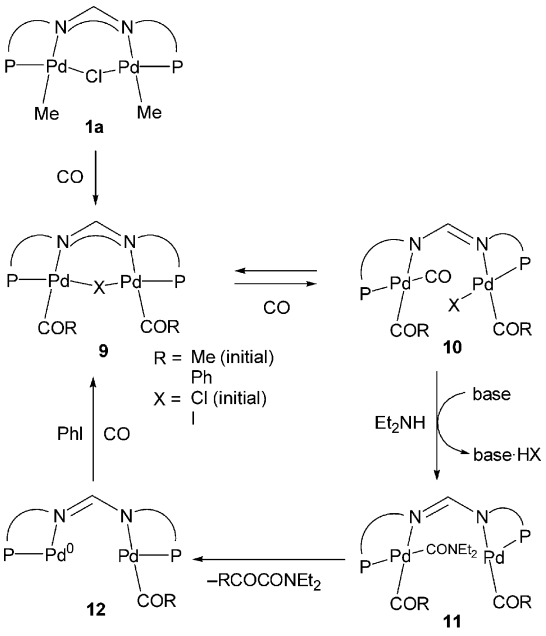
selectivities and fair total yields (entries 1–3). The palladium platinum heterodinuclear complex **2** gave similar good results (entry 4). Chloro-bridged dimethyl diplatinum complex **3** (entry 5) did not express any catalytic activity showing that at least one palladium atom per complex is necessary for the reaction. Dpfam-coordinated mononuclear palladium complex **4** is employed presuming that electronic properties will mimic the half units of the bimetallic complex **1a**. The complex **4** exhibited good results similar to those with dinuclear complex **1a** in terms of selectivity and activity (entry 6). Apparent cooperative effects to improve the efficiency and selectivity associated with the dinuclear complex **1a** are obscure under these reaction conditions. There was some concern that the complex **1a** might fragment completely into its constituent species, i.e. monomeric complex **4** and Pd(Me)Cl, during catalysis at lower concentrations. The results using **1a** and those using **4** would be similar in such a case since Pd(Me)Cl decomposes to metals under the reaction conditions showing sparingly catalytic activity (see Section 4). ^{1}H-NMR analysis of complex **1a** at room temperature in THF-d_8 at the concentration of 1.7×10^{-4} M did not provide any evidence for fragmentation. Some differences between the catalysis of **1a** and that of **4** were revealed under different conditions. Thus, at higher loading concentrations of complex (1%), the dinuclear complex **1a** was more active and selective than the monometallic half unit **4** (entries 7 and 8). The ^{31}P-NMR spectrum of the reaction mixture at the end of the reaction conducted under the same conditions as those in entry 6 in Table 3 showed two singlets at 21.81 and 38.35 ppm together with several small peaks. These values indicate that the phosphorus atoms in the dpfam ligand coordinate to the metal centers since metal-free phosphines resonance in a higher frequency region as is shown for Hdpfam (-19.25 and -15.02 ppm) [14]. Dinuclear complexes and/or mononuclear complexes of the type **4** in which two phosphorus atoms in the dpfam ligand coordinate to the metal center are responsible for the peaks. However, the latter type of complexes should exhibit two sets of doublets resulted from 2-bond PP coupling. For example, the spectrum of **4** shows the peaks at 19.01 and 35.46 ppm ($^{2}J_{pp} = 402$ Hz) [14]. Taking into account the above results and that there was no metal precipitation observed visually for the bimetallic complex **1a**, it may be concluded that there was little or no fragmentation of **1a** during catalysis. Several mononuclear $PdCl_2$-phosphine complexes were tested for comparison with the dinuclear complexes. $PdCl_2(PPh_3)_2$ and $PdCl_2$(dppf) exhibited moderate selectivities (entries 9 and 13). Higher selectivities were realized with diphosphine-coordinated complexes such as $PdCl_2$(dppe), $PdCl_2$(dppp), and $PdCl_2$(dppb) (entries 10–12). Among these monometallic complexes, the dppp-coordinated complex is excellent in terms of selectivity and activity. The efficiency of diphosphine-coordinated palladium complexes on the double carbonylation of iodobenzene has been explored [3].

The mechanism of the double carbonylation catalyzed by a single metal complex proposed previously is shown in Scheme 2. The α-keto amide is produced by attack of the amine on the coordinated carbon monoxide in the aroyl(carbonyl)palladium species **7** followed by reductive elimination. Species **7** may be neutral or ionic depending on the nature of the ligand X and the solvent used [4a]. On the other hand, amide are formed from the aryl(carbonyl)palladium species **8**. We propose a possible mechanism of the double carbonylation catalyzed by the dinuclear complex **1a** in Scheme 3 in which P–N–N–P donates dpfam or an analogous ligand by referring to that presented for a mononuclear complex. The first step is the insertion of carbon monoxide into the palladium–methyl bonds to give the acetyl complex **9**. This step was confirmed independently. When **1a** was allowed to react with 20 atm of carbon monoxide at room temperature, the methyl peak at 0.64 ppm in the ^{1}H-NMR spectrum of the original complex disappeared completely after 16 h and a new peak attributed to the acetyl group appeared at 2.14 ppm. The second step is the coordination of carbon monoxide to **9** giving the species **10**. Nucleophilic attack of diethylamine on the coordinated carbon monoxide ligand in **10** gives rise to an acyl-carbamoyl species **11**, which reductively eliminates α-keto amide and generates $Pd^{0}Pd^{II}$ bimetallic species **12**. The intermediate **12** undergoes oxidative addition with iodobenzene followed by carbon monoxide insertion to afford the acyl species **9** that carries the catalytic cycles.

The selectivity for **6** gradually improved as the ratio of diethylamine to **1a** increased (vide supra). The rate of carbon monoxide insertion (**12** → **9**) may be increased in the environment of amine [22] to generate a benzoylpalladium species, the key intermediate for the forma-



Scheme 2.



Scheme 3.

tion of α-keto amide. And the CO-coordinated species **10** can be efficiently converted into the carbamoyl species **11** by employment of a large diethylamine/catalyst ratio.

3. Conclusion

We have found that dpfam-coordinated dinuclear palladium complexes are very efficient and selective catalysts for the double carbonylation of iodobenzene with diethylamine especially in a lower loading region of the complex using K_3PO_4 as base and 1,4-dioxane as solvent. This catalyst system allows the double carbonylation reaction with a TON up to 10^5 and selectivity of 96%. The involvement of dinuclear species during catalysis has been suggested from the ^{31}P-NMR measurement at the end of the reaction.

4. Experimental

4.1. Materials and methods

Amines, inorganic bases, iodobenzene, 4-iodoanisole, 4-iodotoluene, 4-chloroiodobenzene, 4-iodonitrobenzene, 1-iodonaphthalene, 2-iodopyridine, 3-iodopyridine, and 2-iodothiophene were obtained commercially and used without further purification. 2-Iodonaphthalene [23] and 2-iodofuran [24] were prepared according to published methods. The preparation of the Hdpfam ligand and their dinuclear complexes were reported previously [14]. ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker DPX-400 or a Bruker DRX-500 spectrometer. Infrared spectra were measured on a JEOL FTIR-350. GCMS analyses were performed on a Shimadzu GCMS-QP 5050. GC analyses were carried out with a Shimadzu GC-8A. Elemental analyses were performed by the Microanalytical Laboratory of the Institute of Multidisciplinary Research for Advanced Materials, Tohoku University. α-Keto amides were characterized by means of elemental analysis (C, H, N), IR, ^{1}H-/^{13}C-NMR, GCMS spectroscopy. *N,N*-Diethyl-3-pyridylglyoxamide and *N,N*-diethyl-2-thiophenylglyoxamide were characterized only by ^{1}H-NMR because the yields were very low. The known products were characterized spectroscopically.

4.2. Double carbonylation of aryl iodide catalyzed by a dinuclear complex

The typical procedure (Table 7, entry 1) was as follows. Into a 50 ml stainless-steel pressure bottle, iodobenzene (5.0 mmol), diethylamine (7.5 mmol), K_3PO_4 (5.0 mmol), dinuclear palladium complex **1a** (0.01 mol%), and 1,4-dioxane (3.0 ml) were added under nitrogen atmosphere. Then, carbon monoxide was introduced up to 10 atm at room temperature, and the bottle was heated in an oil bath at 100 °C for 15 h. After reaction, carbon monoxide was purged carefully. The reaction mixture was passed through a short column eluting with diethyl ether to remove palladium complexes and inorganic materials and analyzed by means of GC by using *n*-tetradecane as an internal standard. The α-keto amide and amide produced were isolated by column chromatography (silica gel 60N) eluting with hexane/ethyl acetate.

4.3. Double carbonylation of iodobenzene catalyzed by Pd(Me)Cl(cod)

The carbonylation of iodobenzene (5.0 mmol) with diethylamine (7.5 mmol) were carried out using 1,4-dioxane (5 ml) as solvent and K_3PO_4 (5.0 mmol) as base in the presence of Pd(Me)Cl(cod) (0.01 mol%) at 100 °C for 15 h under 10 atm of carbon monoxide pressure. This procedure afforded **5** and **6** in 18% total yield with 73% selectivity for α-keto amide **6**. There were black precipitations after the reaction.

4.4. ^{31}P-NMR experiment of the reaction mixture at the end of the reaction

The reaction mixture yielded in the reaction under the same conditions as those in entry 6 Table 3 was filtered and washed with 1,4-dioxane. Volatile compounds (iodobenzene, diethylamine, and 1,4-dioxane) were removed from the filtrate under reduced pressure (30 °C,

0.5 mmHg). The $^{31}P\{^{1}H\}$-NMR spectra (162 MHz, $CDCl_3$) of the resulted pale-yellow oil exhibited two singlets at 21.81 and 38.35 ppm.

4.4.1. N,N-Diethyl-4-nitrophenylglyoxamide

Isolated by column chromatography (hexane/ethyl acetate = 1/1). A light orange solid: m.p. 95–96 °C. ^{1}H-NMR ($CDCl_3$): δ 8.35 (dt, $J = 9.0$, 2.0 Hz, 2H), 8.13 (dt, $J = 9.0$, 2.0 Hz, 2H), 3.58 (q, $J = 7.1$ Hz, 2H), 3.27 (q, $J = 7.1$ Hz, 2H), 1.31 (t, $J = 7.1$ Hz, 3H), 1.19 (t, $J = 7.1$ Hz, 3H); ^{13}C-NMR ($CDCl_3$): δ 189.1, 165.4, 151.0, 137.7, 130.7, 124.1, 119.6, 42.2, 39.2, 14.2, 12.8; IR (KBr): 1686, 1638, 1524, 1347, 1224 cm^{-1}; GCMS (70 eV) *m/z* 100 (100), 72 (87), 44 (39); Anal. Calc. for $C_{12}H_{14}N_2O_4$: C, 57.59; H, 5.64; N, 11.19. Found: C, 57.44; H, 5.63; N, 11.14%.

4.4.2. N,N-Diethyl-1-naphthylglyoxamide

Isolated by column chromatography (hexane/ethyl acetate = 2/1). A red solid: m.p. 43–44 °C. ^{1}H-NMR ($CDCl_3$): δ 9.26 (d, $J = 7.7$ Hz, 1H), 8.08 (d, $J = 7.7$ Hz, 1H), 7.99 (d, $J = 7.7$ Hz, 1H), 7.89 (d, $J = 7.7$ Hz, 1H), 7.67 (t, $J = 7.7$ Hz, 1H), 7.57 (t, $J = 7.7$ Hz, 1H), 7.52 (d, $J = 7.7$ Hz, 1H), 3.56 (q, $J = 7.1$ Hz, 2H), 3.29 (q, $J = 7.1$ Hz, 2H), 1.30 (t, $J = 7.1$ Hz, 3H), 1.15 (t, $J = 7.1$ Hz, 3H); ^{13}C-NMR ($CDCl_3$): δ 194.0, 167.1, 135.6, 134.2, 133.9, 130.9, 129.1, 128.6, 128.5, 126.8, 125.7, 124.4, 42.1, 38.7, 13.8, 12.7; IR (KBr): 1670, 1639, 1230, 784 cm^{-1}; GCMS (70 eV) *m/z* 255 (17), 155 (100), 127 (53), 100 (26), 72 (27); Anal. Calc. for $C_{16}H_{17}NO_2$: C, 75.27; H, 6.71; N, 5.49. Found: C, 75.24; H, 6.88; N, 5.44%.

4.4.3. N,N-Diethyl-2-naphthylglyoxamide

Isolated by column chromatography (hexane/ethyl acetate = 2/1). A white solid: m.p. 52–53 °C. ^{1}H-NMR ($CDCl_3$): δ 8.43 (s, 1H), 8.04-7.86 (m, 4H), 3.62 (q, $J =$ 7.2 Hz, 2H), 3.28 (q, $J = 7.2$ Hz, 2H), 1.33 (t, $J = 7.2$ Hz, 3H), 1.16 (t, $J = 7.2$ Hz, 3H); ^{13}C-NMR ($CDCl_3$): δ 191.6, 166.8, 136.2, 132.7, 132.4, 130.6, 129.8, 129.2, 128.9, 127.9, 127.0, 123.7, 42.1, 38.8, 14.1, 12.8; IR (KBr): 1674, 1643, 1461, 1190, 1119, 786 cm^{-1}; GCMS (70 eV) *m/z* 255 (7), 155 (100), 127 (61), 100 (35), 72 (37); Anal. Calc. for $C_{16}H_{17}NO_2$: C, 75.27; H, 6.71; N, 5.49. Found: C, 75.16; H, 6.84; N, 5.45%.

4.4.4. N,N-Diethyl-3-pyridylglyoxamide

Isolated by column chromatography (hexane/ethyl acetate = 10/1). ^{1}H-NMR ($CDCl_3$): δ 9.15 (d, $J = 1.9$ Hz, 1H), 8.87 (dd, $J = 4.8$, 1.9 Hz, 1H), 8.27 (dt, $J = 7.9$, 1.9 Hz, 1H), 7.51 (dd, $J = 7.9$, 4.8 Hz, 1H), 3.59 (q, $J =$ 7.1 Hz, 2H), 3.30 (q, $J = 7.1$ Hz, 2H), 1.32 (t, $J = 7.1$ Hz, 3H), 1.21 (t, $J = 7.1$ Hz, 3H).

4.4.5. N,N-Diethyl-2-thiophenylglyoxamide

Isolated by column chromatography (hexane/ethyl acetate = 2/1). ^{1}H-NMR ($CDCl_3$): δ 8.41 (d, $J = 3.8$ Hz, 1H), 7.83 (d, $J = 3.8$ Hz, 1H), 7.18 (t, $J = 3.8$ Hz, 1H), 3.43 (q, $J = 7.2$ Hz, 4H), 1.25 (t, $J = 7.2$ Hz, 6H).

4.4.6. N,N-Diethyl-2-thiophenylglyoxamide

Isolated by column chromatography (hexane/ethyl acetate = 1/1). Yellow oil. ^{1}H-NMR ($CDCl_3$): δ 8.18 (dd, $J = 2.9$, 1.2 Hz, 1H), 7.58 (dd, $J = 5.2$, 1.2 Hz, 1H), 7.36 (dd, $J = 5.2$, 2.9 Hz, 1H), 3.53 (q, $J = 7.1$ Hz, 2H), 3.28 (q, $J = 7.1$ Hz, 2H), 1.27 (t, $J = 7.1$ Hz, 3H), 1.18 (t, $J = 7.1$ Hz, 3H); ^{13}C-NMR (CDCl3): δ 185.1, 166.5, 138.7, 136.1, 127.0, 126.9, 42.2, 39.0, 14.2, 12.7. IR (neat): 1669, 1638, 1240, 1140 cm^{-1}; GCMS (70 eV) *m/z* 111 (52), 100 (72), 72 (100), 44 (37), 39 (49); Anal. Calc. for $C_{10}H_{13}NO_2S$: C, 56.85; H, 6.20; N, 6.63; S, 15.18. Found: C, 56.58; H, 6.08; N, 6.33; S, 15.25%.

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