Carboxylation of gaseous alkanes with CO catalyzed by Pd-Cu-based catalysts: a spectroscopic study

Kazuyuki Nakata, Tsutomu Miyata, Yuki Taniguchi, Ken Takaki, Yuzo Fujiwara *

Department of Applied Chemistry, Faculty of Engineering, Hiroshima University, Kagamiyama, Higashi-Hiroshima 724, Japan

Abstract

The $Pd(OAc)_2$–$Cu(OAc)_2$–$K_2S_2O_8$–CF_3COOH (TFA) system causes the carboxylation of small alkanes such as methane, ethane and propane under mild conditions to give the corresponding carboxylic acids with high yields. The interaction between $Pd(OAc)_2$ and $Cu(OAc)_2$ in TFA was studied by visible–UV spectroscopy, electron spectroscopy for chemical analysis (ECSA), and ^{19}F NMR measurements. It was found that in this system $Pd(OCOCF_3)_2$ and $Cu(OCOCF_3)_2$ could be generated in situ and then the Pd–Cu (1:1) complex would be formed in which Pd was more positive than that in $Pd(OAc)_2$ alone. The Cu salt plays an important role of strengthening the electrophilicity of $Pd(OAc)_2$.

Keywords: Palladium; Methane; GH activation; Alkanes; Propane; Vis-UV

1. Introduction

Alkanes, particularly methane, are the most abundant natural source of organic molecules on the earth, and therefore their effective utilization is of great interest not only in scientific but also in industrial fields. In previous papers [1–4], we have reported that the Pd–Cu-catalyzed direct carboxylation of small alkanes such as methane, ethane and propane proceeds electrophilically to give the corresponding carboxylic acids with high yields (Scheme 1). In the reaction, the combination of $Pd(OAc)_2$ and $Cu(OAc)_2$ gives the best results, and $Pd(OAc)_2$ alone gives inferior yields. Interestingly, this direct carboxylation reaction proceeds only when the ratio of Cu to Pd is more than unity. However, the role of the Cu salt in this system remains unknown. In order to clarify the role of the Cu salt and to obtain information about the active species of the carboxylation reaction, we investigated the interaction between the Pd and Cu salts in the Pd–Cu mixed-catalyst system in trifluoroacetic acid (TFA) by visible–UV spectroscopy, electron spectroscopy for chemical analysis (ESCA) and ^{19}F NMR spectroscopy measure-

ments. Some preliminary results have been published elsewhere [5].

2. Results and discussion

First, we have investigated the carboxylation reaction of propane (10 atm) with CO (20 atm) using $K_2S_2O_8$ and various Pd and Cu salts as catalysts. Table 1 summarizes the results, and the data in the table indicate that the combination of both Pd and Cu such as Pd(0)–Cu(II) (Table 1, runs 1 and 2), Pd(II)–Cu(0) (Table 1, run 7) and Pd(II)–Cu(I) (Table 1, run 6) are all effective as well as Pd(II)–Cu(II) (Table 1, runs 4 and 5) for the butyric acid synthesis. From these results, on can see that any combination of the Pd and Cu salts is effective for the reaction and that Pd alone gives an inferior yield (Table 1, run 3). This suggests that some active species containing the Pd and Cu salts would be formed in situ to accelerate the reaction.

Since both oxidizing and reducing agents such as $K_2S_2O_8$ and CO exist in this system, the valence number of metal salts will be changed. The ligand of Pd and Cu salts would be exchanged from acetate to trifluoroacetate.

Thus we investigated the oxidation states of the Pd and Cu salts after the reaction by ESCA. The samples

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* Corresponding author.
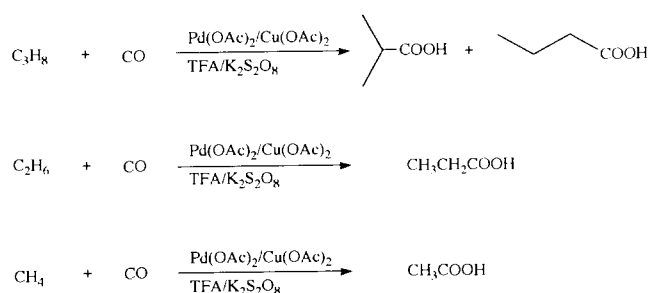
Scheme 1.

were prepared from the reaction mixture by evapora-
tion of the solvent in vacuo after the reaction. The
results are shown in Table 2. The most interesting
result is that, in the case where Pd and Cu salts coexist,
Cu(II) is reduced to univalent, and zero-valent Pd (Pd
black) is oxidized to divalent (Table 2, runs 1 and 2) [6].
Since in the presence of $K_2S_2O_8$, the oxidizing agent
Cu(II) is not reduced even if CO coexists (Table 2, run
3), there could be an interaction between Pd(II) and
Cu(II) salts in which Cu(II) is reduced to Cu(I), making
Pd(II) more positive. However, it seems that Cu(II)
alone cannot oxidize Pd black (Table 2, run 4).

Furthermore, in order to investigate the effect of
$Cu(OAc)_2$ on the reactivity of $Pd(OAc)_2$, we examined
the absorption maximum (λ_{max}) by the visible–UV
spectroscopy measurement. The λ_{max} of $Pd(OAc)_2$ in
TFA occurs at 406 nm (Fig. 1, curve b). Interestingly,
the addition of an equimolar amount of $Cu(OAc)_2$
resulted in a blue shift $(\lambda_{max} = 369$ nm) as shown in
Fig. 1, curve a.

In addition, we investigated the effect of the Cu-to-
Pd ratio on the λ_{max} of Pd and Cu acetates. The results
are shown in Table 3. The TFA solutions of $Pd(OAc)_2$
and $Cu(OAc)_2$ exhibit their absorption maxima λ_{max} at
406 nm and 727 nm respectively (Table 3, runs 1 and
6). However, in the mixture of the Pd and Cu acetates,
the λ_{max} of Pd and Cu acetates shifted depending upon
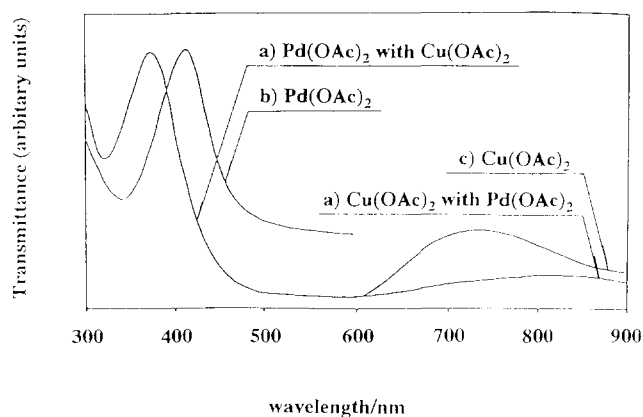the ratio of these two components. As the ratio of Cu

Fig. 1. UV spectra of Pd/Cu mixed catalyst. (a) $Pd(OAc)_2$ 0.05
mmol, $Cu(OAc)_2$ 0.05 mmol in TFA 10 ml. (b) $Pd(OAc)_2$ 0.05 mmol
in THC 10 ml. (c) $Cu(OAc)_2$ 0.05 mmol in TFA 10 ml.

to Pd increased, the λ_{max} of the Pd salt shifted to
shorter wavelengths with a red shift of that of the Cu
salt and finally reached 369 nm when the amount of
$Cu(OAc)_2$ is equal to that of $Pd(OAc)_2$; further addi-
tions of $Cu(OAc)_2$ had no effect on λ_{max} of the Pd salt
(Table 3, runs 4 and 5). The present carboxylation
reaction proceeds most efficiently only when an amount
of $Cu(OAc)_2$ equimolar or more to that of $Pd(OAc)_2$ is
used [1–4]. Therefore it seems that the Cu salt has
some electronic influence on the Pd salt, making Pd
more positive. Thus these results of the visible–UV
measurements correspond to the reactivity of the Pd–
Cu catalyst in these carboxylation reactions. It seems
that a Pd–Cu (1 : 1) complex is formed in which Pd is
more positive than that of $Pd(OAc)_2$ alone if the ratio
of Cu to Pd is more than unity.

Fig. 2 shows the effect of the ratio of $Cu(OAc)_2$ to
$Pd(OAc)_2$ on the yield of butyric acids in the reaction
of propane with CO. As is apparent from Fig. 2, only
when the λ_{max} of the Pd salt is 369 nm, does the
reaction proceed efficiently. Contrary to this, when the
λ_{max} of Pd is not 369 nm, the yield is very low. An
amount of the Cu salt equal or more to that of the Pd
salt is necessary for a high yield. Fig. 3 shows the effect
of the ratio of $Pd(OAc)_2$ to $Cu(OAc)_2$ on the reaction
yield based on propane. In the presence of an excess
amount of $Cu(OAc)_2$ the yield increases in proportion
to the amount of $Pd(OAc)_2$ since the concentration of
active species increases with increasing amount of
$Pd(OAc)_2$. In this region the λ_{max} of the Pd salt is 369
nm. When the ratio of Pd to Cu becomes greater than
unity, the reactivity decreases dramatically and in this
region the λ_{max} of Pd salt is more than 369 nm. From
these results, one can see that the λ_{max} of the active
species is 369 nm and that the active species of this
reaction would be a Pd–Cu (1 : 1) complex.

Next, in order to clarify the mechanism of the shift,
the time course of the λ_{max} of $Pd(OAc)_2$ in TFA was
investigated. The results are shown in Fig. 4. In the

Table 1
Reaction of propane with CO by Pd–Cu-based catalysts (Reaction
conditions: propane, 10 atm; CO, 20 atm; catalyst, 0.05 mmol each;
$K_2S_2O_8$, 9 mmol; TFA, 5 ml; at 80°C for 20 h)

Run	Catalyst	Product (Yield [a] (%))	
		Isobutyric acid	Butyric acid
1	Pd black–$Cu(OAc)_2$	4200 (5.1)	1100 (1.3)
2	Pd black–$CuCl_2$	6100 (7.5)	1500 (1.9)
3	Pd black	360 (0.4)	110 (0.1)
4	$Pd(OAc)_2$–$Cu(OAc)_2$	5500 (6.7)	1600 (2.0)
5	$Pd(OAc)_2$–$CuCl_2$	6100 (7.5)	1400 (1.7)
6	$Pd(OAc)_2$–CuCl	5400 (6.6)	1400 (1.7)
7	$Pd(OAc)_2$–Cu powder	5600 (6.9)	1400 (1.7)

[a] Gas chromotography (GC) yield based on catalyst (on propane).

Table 2
Analysis of oxidation states of Pd and Cu salts by electron spectroscopy for chemical analysis

Run	Oxidation state of starting materials		Conditions [a]		Resulting materials			
	Pd [b]	Cu [c]	$K_2S_2O_8$	CO	Binding energy (eV)		Assgined oxidation state	
					Pd $3d_{5/2}$	Cu $2p_{3/2}$	Pd	Cu
1	II	II	Yes	Yes	338.4	931.6	II	I
2	0	II	Yes	Yes	337.8	932.4	II	I
3	–	II	Yes	Yes	—	935.9	—	II
4	0	II	No	No	335.7	935.3	0	II

[a] $K_2S_2O_8$, 9 mmol; CO, 20 atm; at 80°C for 5 h.
[b] Pd(OAc)$_2$ or Pd black, 1 mmol.
[c] Cu(OAc)$_2$, 1 mmol for runs 1, 2, and 3; 2 mmol for run 4.

case of Pd(OAc)$_2$ alone, the λ_{max} of the Pd salt did not shift at all. When the ratio of Cu to Pd is 0.25, the rate of shift is very slow, and the λ_{max} of the Pd salt cannot reach 369 nm, because the λ_{max} of the Pd salt reaches 369 nm only when the ratio of Cu to Pd is more than unity. In the cases when the Cu-to-Pd ratio is more than unity, the shift rate of the λ_{max} of the Pd salt is controlled by the amount of Cu salt. Excess amounts of Cu(OAc)$_2$ accelerate the shift rate. When the amount of Cu salt was four times that of the Pd salt, the time required for the formation of the active species was only about 30 min, which is a quarter of that when the ratio of Cu to Pd is unity. From these results, one can see that the shift rate of the λ_{max} of the Pd salt is influenced by the ratio of Cu to Pd. However, from the final λ_{max} of the Pd salt (369 nm), the active species formed in each system would be actually the same.

Furthermore, the effect of the concentration of Pd(OAc)$_2$ in TFA in various Cu to Pd ratios on the shift of the λ_{max} of the Pd was investigated. The results are shown in Fig. 5. Interestingly enough, the concentration of the Pd salt does not influence the shift at all. The shift rate of the λ_{max} of the Pd salt is controlled only by the ratio of Cu to Pd.

Finally, we investigated the ligand of Pd and Cu in the active species. Pd(OCOCF$_3$)$_2$ and Cu(OCOCF$_3$)$_2$ (0.05 mmol each) prepared by the literature procedure [8] were dissolved in TFA (10 ml), and the TFA solution was stirred at 80°C for 40 h. Then visible–UV

measurements of this solution were carried out. As a result, the λ_{max} values at 369 nm and 818 nm due to the Pd and Cu salts respectively were observed, which are in agreement with the signals of the active species.
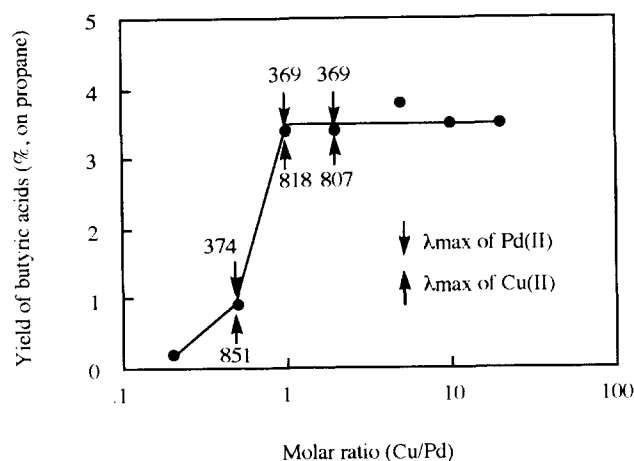

Fig. 2. Plot of the yield of butyric acids vs. the ratio of Cu(OAc)$_2$ / Pd(OAc)$_2$. Conditions Pd(OAc)$_2$ 0.05 mmol, K$_2$S$_2$ 0.89 mmol, TFA 5 ml propane 10 atm, CO 20 atm, 80°C, 5 h.
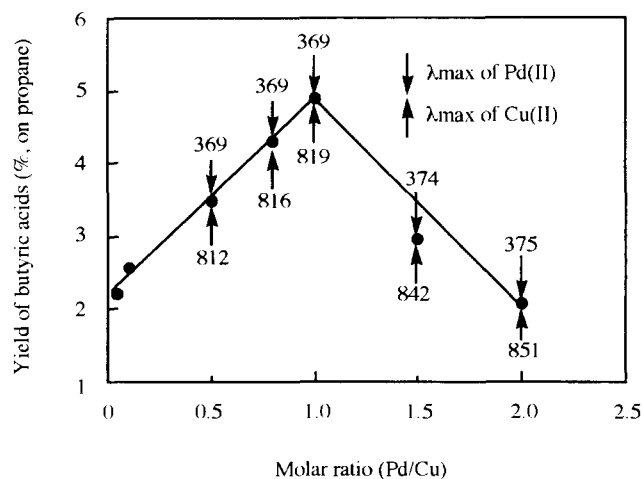
Table 3
Visible–UV spectra of a mixture of Pd(OAc)$_2$ and Cu(OAc)$_2$. (Measured after stirring of Pd(OAc)$_2$ (0.05 mmol) and Cu(OAc)$_2$ in TFA (5 ml) at room temperature for 50 h)

Run	Molar ratio of Cu to Pd	λ_{max} (nm)	
		Pd(II)	Cu(II)
1	Pd(II) only	406	—
2	0.5	375	851
3	0.7	374	841
4	1.0	369	818
5	1.5	369	812
6	2.0	369	807
7	Cu(II) only	—	727

Fig. 3. Plot of the yield of butyric acid vs. the ratio of Pd(OAc)$_2$ / Cu(OAc)$_2$. Conditions: Cu(OAc)$_2$ 0.5 mmol, K$_2$S$_2$O$_8$ 9 mmol, TFA 5 ml, propane 10 atm, CO 20 atm, 80°C, 5 h.
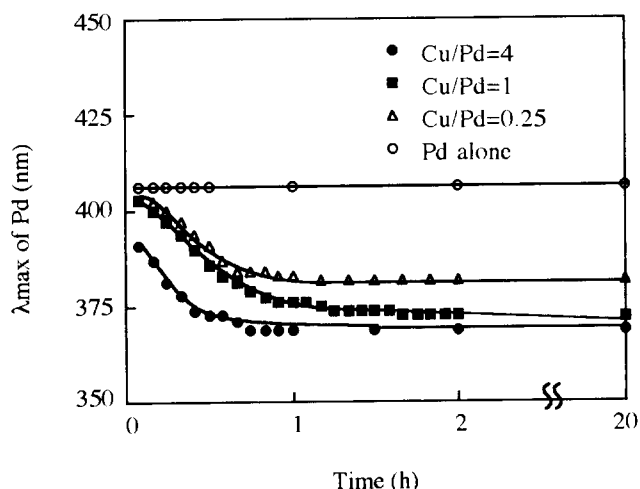
Fig. 4. Time course of the shift of the λ_{max} of Pd(OAc)$_2$ in TFA. Conditions: total amount of Pd(OAc)$_2$ and Cu(OAc)$_2$ 0.05 mmol, TFA 10 ml, rt.
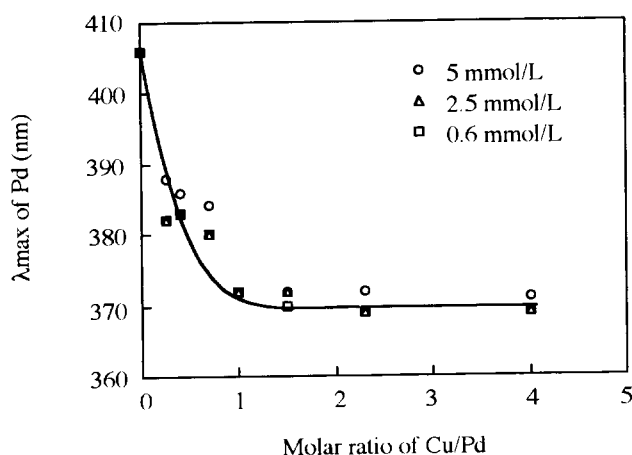

Fig. 5. Plot of the λ_{max} of Pd vs. the ratio of Pd(OAc)$_2$/Cu(OAc)$_2$ in various concentrations. Conditions: o: Pd(OAc)$_2$ and Cu(OAc)$_2$ 0.025 mmol each, TFA 5 ml, △; Pd(OAc)$_2$ and Cu(OAc)$_2$ 0.0125 mmol each, TFA 5 ml, □: Pd(OAc)$_2$ and Co(OAc)$_2$ 0.003 mmol each, TFA 5 ml.

This clearly indicates that the ligand of both Pd and Cu in the active species is trifluoroacetate.

Since it became apparent that the ligand of the active species was trifluoroacetate, we tried to clarify the reason why the λ_{max} of the Pd salt shifted in the presence of the Cu salt by means of ^{19}F NMR measurements. The signals of Pd(OCOCF$_3$)$_2$ and Cu(OC-OCF$_3$)$_2$ are observed at 120.95 ppm and 166.99 ppm respectively. However, in the Pd(OAc)$_2$–Cu(OAc)$_2$ (1:1) mixed catalyst system in TFA, the signal of Cu shifted to 135.12 ppm while a little shift of that of Pd was observed (to 121.95–123.24 ppm, complex signals). These results seem to show that the fluorine atom on the ligand of Cu becomes electron rich, and the electron on Pd is transferred into the Cu side. Thus the electron density on Pd decreases and the electrophilicity of Pd increases. As a result, the combination of an

equal amount of Pd(OAc)$_2$ and Cu(OAc)$_2$ gives the best reactivity for the carboxylation of alkanes with CO.

3. Conclusions

The Pd–Cu mixed catalyst in TFA promotes the carboxylation of alkanes with CO efficiently. The λ_{max} of the active species of the reaction is 369 nm which is derived from the shift caused by the Cu salt from 406 nm of Pd alone. Only if the ratio of Cu to Pd is more than unity, is this active species, the Pd–Cu (1:1) complex, formed. Since the electron density of Pd in this Pd–Cu (1:1) complex is lower than that of the free Pd salt, this active species has a higher electrophilicity to accelerate the carboxylation reactions and gives rise to carboxylic acids with high yields.

4. Experimental section

4.1. Materials and methods

Mass spectra were obtained on a Shimadzu GC-MS QP1000 spectrometer. GC analyses were performed on a Shimadzu GC-8A equipped with a Thermal Conductivity detector or a flame ionization detector with a 1 m column of 3.2 mm inside diameter consisting of 10% polyethylene glycol 6000 on Chromosorb W for the analyses of liquid layer. Visible–UV spectra were obtained on a Jasco Unidec-610A spectrophotometer. ESCA data were obtained on Perkin–Elmer ESCA5400 MC. ^{19}F NMR spectra were obtained on a Bruker AM-X 400wb spectrometer. Propane gas (Sumitomo Pure Chemical Co.), carbon monoxide (Sumitomo Pure Chemical Co.) and trifluoroacetic acid (Waco Chemical Co.) were used without purification. Pd(OAc)$_2$ was prepared by the literature procedure [8]. Cu(OAc)$_2$ and other metal salts were purchased (Waco) and dried by azeotropic distillation with benzene.

4.2. Identification of the products and determination of the yield

The products were identified by comparison of GC, GC mass spectroscopy and NMR spectra with those of commercially available authentic samples. The yields of butyric and isobutyric acids were determined by gas–liquid chromatography (GLC) using pentanoic acid as an internal standard.

4.3. Reaction of propane with CO by the Pd–Cu-based catalyst

A 50 ml glass centrifuge tube equipped with a Teflon-covered magnetic stirring bar was charged with

catalysts and the solvent as shown in Table 1. The solution was stirred for 5 min. Then $K_2S_2O_8$ (2.43 g, 9 mmol) was added to the solution. A rubber septum with a glass needle was fitted to a tube, which was placed in a 100 ml stainless steel autoclave. The autoclave was closed, flushed with propane and pressurized to 10 atm with propane and 20 atm with CO. The mixture was heated with stirring at 80°C for 20 h. After cooling and venting of the residual gas, the autoclave was opened and the mixture was analyzed directly by GLC without aqueous work-up using pentanoic acid as an internal standard to give butyric acids with 7100% yield.

4.4. Preparation of samples for electron spectroscopy for chemical analysis measurement

In a 50 ml glass centrifuge tube placed in a stainless steel autoclave, $Pd(OAc)_2$ (224 mg, 1 mmol), $Cu(OAc)_2$ (183 mg, 1 mmol), $K_2S_2O_8$ (2.43 g, 9 mmol) and TFA (5 ml) were stirred at 80°C for 5 h under CO at 20 atm. After the reaction the solvent was removed from reaction mixture and the residue dried in vacuo to give a powder. Thin film was made from the powder obtained. ESCA was conducted using a magnesium $K\alpha$ (1254.6 eV) source. The binding energies of metals were determined on the basis of C 1s peak (284.6 eV). These results are listed in Table 2.

4.5. Visible–UV spectroscopy measurement

In a 50 ml round-bottomed flask, $Pd(OAc)_2$ (0.05 mmol) and $Cu(OAc)_2$ (appropriate amounts) were dissolved in TFA (5 ml) as in Table 3. The solution was stirred at room temperature for 50 h, and then visible–UV measurements of the solution were done with a Jasco Unidec-610A spectrophotometer using a quartz cell. $Pd(OAc)_2$ and $Cu(OAc)_2$ in TFA have λ_{max} values of 406 nm and 727 nm respectively.

4.6. Effect of the ratio of Cu to Pd on the yield of butyric acids

The reactions were carried out as described above using $Pd(OAc)_2$ (11.2 mg, 0.05 mmol), $Cu(OAc)_2$ (appropriate amounts), $K_2S_2O_8$ (2.43 g, 9 mmol) and TFA (5 ml). Subsequently the reaction products were analyzed directly by GLC without aqueous work-up using pentanoic acid as an internal standard. These results

for the Cu-to-Pd ratio (yields based on propane) are as follows and are shown in Fig. 2: 20 (3.5%), 10 (3.5%), 5 (3.8%), 2 (3.4%), 1 (3.4%), 0.5 (0.9%), 0.2 (0.2%).

4.7. ^{19}F NMR measurement

In a 50 ml round-bottomed flask, $Pd(OAc)_2$ (224 mg, 1 mmol) and $Cu(OAc)_2$ (186 mg, 1 mmol) were dissolved in TFA (5 ml). After stirring at room temperature for 24 h, a gray precipitate was obtained. The sample of the precipitate of a mixture of $Pd(OCOCF_3)_2$ and $Cu(OCOCF_3)_2$ was prepared. An acetone-d_6 solution of the sample was analyzed by ^{19}F NMR measurements using α, α, α-trifluorotoluene as an external standard. Optical spectroscopy data of the precipitate of a mixture of Pd and Cu salts were as follows: 121.95–123.24 ppm (Pd in the precipitate, complex peaks), 135.12 ppm (Cu in the precipitate, brs), 120.95 ppm ($Pd(OCOCF_3)_2$, s), and 166.99 ppm ($Cu(OCO-CF_3)_2$, brs).

References and notes

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