chromatography (solvent gradient, CH_2Cl_2/EtOAc (2:1 to 1:1)) and gave a yellow solid (53 mg). Recrystallization from MeOH gave **22** as yellow needles: mp 190-192 °C dec; ^1H NMR (see Table I); CIMS, *m/e* (relative intensity) 278 (M + 1, 100), 277 (14), 276 (11), 260 (60); UV spectrum in MeOH (λ_{max}, nm (ϵ_{max})) 255 (41 500), 280 (48 000), 288 (43 000), 344 (4000 sh), 363 (8200), 381 (11 300). Anal. Calcd for $C_{18}H_{15}NO_2$: C, 77.96; H, 5.45; N, 5.05. Found: C, 77.68; H, 5.48; N, 4.97.

***trans*-3,4-Dihydro-3,4-dihydroxy-7-methylbenz[*c*]acridine (24).** Similar treatment of **23** (38 mg) gave a yellow solid which on fractionation by PLC (three plates, 20 × 20 cm, CH_2Cl_2/EtOAc, 1:1) gave **24** (20 mg). Recrystallization from EtOAc gave pale yellow needles: mp 186-191 ° dec; ^1H NMR (see Table I); CIMS, *m/e* (relative intensity) 278 (M + 1, 45), 277 (14), 276 (4), 260 (100); UV spectrum in MeOH (λ_{max}, nm (ϵ_{max})) 261 (103 000), 348 (5600), 366 (9900), 393 (6700); high-resolution electron impact MS, *m/e* 277.1111 ($C_{18}H_{15}NO_2$ requires 277.1102). In dilute MeOH solution **24** was unstable when exposed to white fluorescent light ($t_{1/2}$ ~ 1 h).

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Registry No. **2**, 3340-94-1; **3**, 86538-46-7; **4**, 86538-47-8; **5**, 92145-10-3; **6**, 92145-11-4; **7**, 92145-12-5; **8**, 92145-13-6; **9**, 92145-14-7; **10**, 92145-15-8; **11**, 92145-16-9; **12**, 92145-17-0; **13**, 82962-56-9; **14**, 92145-18-1; **15**, 92145-19-2; **16**, 88797-47-1; **17**, 92145-20-5; **18**, 92145-21-6; **19**, 92145-22-7; **20**, 92145-23-8; **21**, 92145-24-9; **22**, 88797-48-2; **23**, 92145-25-0; **24**, 92145-26-1; **25**, 92145-27-2; **26**, 92145-28-3; **27**, 92145-29-4; **28**, 92145-30-7; **29**, 86538-51-4; **30**, 83876-60-2; **31**, 83876-62-4; *trans*-9-acetoxy-8-(formyloxy)-7-methyl-8,9,10,11-tetrahydrobenz[*c*]acridine, 92145-09-0; ($8\alpha,10\beta,11\alpha$)-8-bromo-10,11-diacetoxy-7-methyl-8,9,10,11-tetrahydrobenz[*c*]acridine, 92145-31-8.

Supplementary Material Available: ^{13}C NMR data for **2-7 10-12**, **14**, **15**, **17-19**, **21**, and **23** (Table II) (2 pages). Ordering information is given on any current masthead page.

Platinum Complex Catalyzed Reductive N-Acylation of Nitro Compounds

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Aromatic and aliphatic nitro compounds reacted with carboxylic acids at 180 °C for 4 h in the presence of a catalytic amount of $PtCl_2(PPh_3)_2$ combined with tin(IV) chloride under 60 atm of carbon monoxide pressure to give corresponding N-substituted amides in moderate to fairly good yields. From nitrobenzene, acetanilide was obtained in 91% yield. Tin(IV) chloride can be substituted by other Lewis acids such as $SnCl_2$, $FeCl_3$, VCl_3, $AlCl_3$, and $ZnCl_2$. The reaction appears to include the formation of nitrene and isocyanate as key intermediates.

One of the most widely applicable methods of amide formation is an acylation of primary or secondary amine with an acylating agent, R^1COX, where X = halogen, R^1COO, R^2O, R^2R^3N, N_3, or BF_4.[1] On the other hand, several attempts have been made in order to prepare amide derivatives from nitro compounds. This so-called reductive N-acylation seems more important industrially for aromatic nitro compounds. These direct anilide formations from nitroarenes were attained by employing various reducing agents. Ho utilized molybdenum hexacarbonyl ($Mo(CO)_6$) as the reducing agent.[2] This reaction, however, required excess $Mo(CO)_6$ (2.0 equiv) and a long reaction time (20 h at 120 °C). Owsley et al. employed metallic iron and succeeded in dissolving iron salts after the reaction.[3] Furthermore, a patent literature claimed that a large excess of acetic acid (40 equiv) reduced nitrobenzene to afford acetanilide at 250 °C.[4] As for catalytic reaction, Kajimoto and Tsuji investigated the anilide formation under carbon monoxide pressure in the presence of group VIII first-row transition-metal-carbonyl catalysts. The reaction proceeded readily at temperatures higher than 300 °C, while the anilides were not obtained at all at 285 °C.[5]

Table I. Reductive N-Acylation of Nitrobenzene Catalyzed by Pt Complexes[a]

run	platinum complex	Lewis acid	CO, atm	convn,[b] %	yield,[b] % acetanilide	aniline
1			0	0	0	0
2			60	0	0	0
3		$SnCl_4$	60	0	0	0
4	$PtCl_2(PPh_3)_2$		60	81	46	18
5	$PtCl_2(PPh_3)_2$	$SnCl_4$	0	0	0	0
6	$PtCl_2(PPh_3)_2$	$SnCl_4$	30	60	29	17
7	$PtCl_2(PPh_3)_2$	$SnCl_4$	60	100	91	0
8[c]	$PtCl_2(PPh_3)_2$	$SnCl_4$	60	100	77	8
9[d]	$PtCl_2(PPh_3)_2$	$SnCl_4$	60	100	59	28
10	$PtCl_2(PhCN)_2$	$SnCl_4$	60	100	59	5

[a] A mixture of nitrobenzene (10 mmol), acetic acid (40 mmol), platinum complex (0.1 mmol), $SnCl_4$ (1.0 mmol), and dioxane (18 mL) was stirred at 180 °C for 4 h. [b] Determined by GLC based on the amount of nitrobenzene charged. [c] Triethylamine (1.8 mmol) was added. [d] H_2O (1.0 mL) was added.

In this paper, we report an alternative catalytic system for the synthesis of N-substituted amides from aromatic or aliphatic nitro compounds under carbon monoxide pressure.

Results

The platinum complex-tin(IV) chloride system showed much higher catalytic activity than that of the catalyst

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Table II. Reductive N-Acylation of Nitrobenzene Catalyzed by Pt Complexes. Effect of Added Phosphorus(III) Ligands and Lewis Acids[a]

run	platinum complex	added ligand	Lewis acid	convn,[b] %	yield,[b] % acetanilide	aniline
10	$PtCl_2(PhCN)_2$		$SnCl_4$	100	59	5
11	$PtCl_2(PhCN)_2$	PPh_3	$SnCl_4$	100	89	7
12	$PtCl_2(PhCN)_2$	P(*o*-Tol)$_3$	$SnCl_4$	100	80	8
13	$PtCl_2(PhCN)_2$	P(*n*-Bu)$_3$	$SnCl_4$	82	45	25
14	$PtCl_2(PhCN)_2$	$Ph_2PCH_2CH_2PPh_2$	$SnCl_4$	39	21	18
4	$PtCl_2(PPh_3)_2$			81	46	18
7	$PtCl_2(PPh_3)_2$		$SnCl_4$	100	91	0
15	$PtCl_2(PPh_3)_2$		$SnCl_4$[c]	100	95	5
16	$PtCl_2(PPh_3)_2$		$SnCl_2$	95	75	4
17	$PtCl_2(Ph_3)_2$		$SnCl_2$[d]	100	73	27
18	$PtCl_2(PPh_3)_2$		$FeCl_3$	100	84	16
19	$PtCl_2(PPh_3)_2$		VCl_3	100	77	23
20	$PtCl_2(PPh_3)_2$		$AlCl_3$	100	75	25
21	$PtCl_2(PPh_3)_2$		$ZnCl_2$	100	73	26

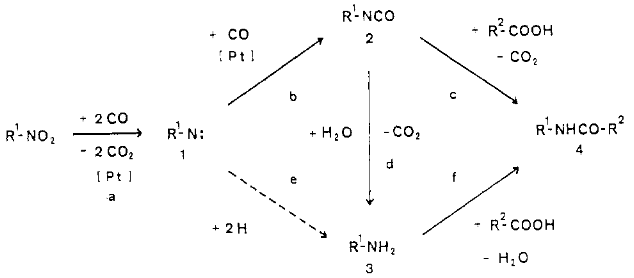
[a] A mixture of nitrobenzene (10 mmol), acetic acid (40 mmol), platinum complex (0.1 mmol), phosphorus(III) ligand (0.25 mmol), Lewis acid (1.0 mmol), and dioxane (18 mL) was stirred at 180 °C for 4 h under carbon monoxide of 60 atm. [b] Determined by GLC based on the amount of nitrobenzene charged. [c] 0.5 mmol. [d] 0.1 mmol.

Table III. Reductive N-Acylation of Nitrobenzene Catalyzed by Pt Complexes. Effect of Reaction Temperature[a]

run	reactn temp, °C	solvent	convn,[b] %	yield,[b] % acetanilide	aniline
22	140	dioxane	0	0	0
23[c]	140	dioxane	26	0	16
24	160	dioxane	23	0	trace
25	160	benzene	63	41	23
26[d]	160	dioxane	57	26	18
7	180	dioxane	100	91	0

[a] A mixture of nitrobenzene (10 mmol), acetic acid (40 mmol), $PtCl_2(PPh_3)_2$ (0.1 mmol), $SnCl_4$ (1.0 mmol), and solvent (18 mL) was stirred for 4 h under carbon monoxide of 60 atm. [b] Determined by GLC based on the amount of nitrobenzene charged. [c] For 10 h. [d] $PtCl_2(PhCN)_2$ (0.1 mmol)–P(*o*-Tol)$_3$ (0.25 mmol) as a catalyst precursor.

Scheme I



system previously reported.[5] Nitro compounds were reductively N-acylated to give N-substituted amides under carbon monoxide pressure in the presence of the platinum catalyst system (eq 1).

$$R^1NO_2 + R^2COOH + 3CO \xrightarrow[180\ °C,\ 4\ h]{[Pt-Sn]} R^1NHCOR^2 + 3CO_2 \quad (1)$$

A series of reactions was performed in order to determine the requirement for high activity of complex catalysts.

Effect of the Component in the Catalyst System. Both platinum complex and carbon monoxide are essential for this reaction (Table I). If one of these components were eliminated from the catalyst system, the reaction did not proceed at all (runs 1, 2, 3, and 5). In the absence of the Lewis acid, the selectivity to acetanilide was low (run 4), while acetanilide was obtained in an excellent yield when the Lewis acid was added to the catalyst system (run 7). Addition of triethylamine and water reduced the yield of acetanilide (runs 8 and 9). Employment of the platinum complex without phosphorus(III) ligands decreased the selectivity to acetanilide (run 10).

It is well-known that phosphorus(III) ligands modify or improve activities of transition-metal catalysts.[6] Triphenylphosphine (cone angle 148°;[7a] pK_a 2.73[7b]) is the most effective for this reaction (Table II). The catalyst system of $PtCl_2(PhCN)_2$ combined with PPh_3 showed an activity comparable to that of $PtCl_2(PPh_3)_2$, indicating that PhCN ligand is readily substituted by the added phosphorus(III) ligand. Tri-*o*-tolylphosphine (P(*o*-Tol)$_3$, which has a larger steric bulkiness, cone angle 194°[7a]) showed the comparable effectiveness to triphenylphosphine. However, tributylphosphine, a more basic ligand (pK_a 7.97[7b]), and a chelating diphosphorus(III) ligand reduced the catalytic activity (runs 13 and 14). The bidentate ligand forms a thermodynamically stable complex with the platinum catalyst, and such a rigid complex seems unfavorable as a catalyst.

In the reaction, the presence of the Lewis acid enhances the yield and the selectivity of acetanilide. Among the Lewis acids employed, tin(IV) chloride gave the best results (runs 7 and 15). For the platinum-catalyzed hydroformylation[8] and hydroesterification,[9] only tin(II) chloride was effective as a cocatalyst. In these reactions, tin(II) chloride worked as a supplier of $SnCl_3^-$ ligand, as fully studied by Anderson and co-workers.[10] However, in the present reaction, various Lewis acids such as $SnCl_2$, $FeCl_3$, VCl_3, $AlCl_3$, and $ZnCl_2$ also enhanced the catalytic activities. Thus the role of Lewis acid seems to be distinct from the preceding studies[8,9] (vide infra). In addition, a 10:1 molar ratio of the Lewis acid to the platinum could be

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Table IV. Reaction with Various Nitro Compounds and Carboxylic Acids[a]

run	nitro compound	carboxylic acid	product	yield,[b] %
27	nitrobenzene	propionic acid	*N*-phenylpropanamide	91 (61)
28	nitrobenzene	succinic acid	*N*-phenylsuccinimide	(30)
29	*p*-nitrotoluene	acetic acid	*N*-(4-methylphenyl)acetamide	85 (52)
30	*p*-nitrochlorobenzene	acetic acid	*N*-(4-chlorophenyl)acetamide	75 (47)
31	*p*-nitroanisole	acetic acid	*N*-(4-methoxyphenyl)acetamide	72 (39)
32[c]	1-nitropropane	acetic acid	*N*-propylacetamide	57
33[d]	1-nitropropane	acetic acid	*N*-propylacetamide	40
34[c]	1-nitrohexane	acetic acid	*N*-hexylacetamide	32

[a] A mixture of nitro compound (10 mmol), carboxylic acid (40 mmol), $PtCl_2(PPh_3)_2$ (0.1 mmol), $SnCl_4$ (1.0 mmol), and solvent (18 mL; dioxane or benzene) was stirred at 180 °C for 4 h under carbon monoxide of 60 atm. [b] Determined by GLC based on the amount of nitro compound charged and figures in the parentheses show isolated yields. [c] Reaction at 150 °C. [d] Reaction at 180 °C.

reduced to 5 (run 15), still more to 1 (run 17) with maintaining the catalytic activities.

For the present synthesis, a reaction temperature higher than 180 °C was necessary (Table III). Lower reaction temperatures reduced the conversion and the yield drastically.

Reaction with Various Nitro Compounds and Carboxylic Acids. Propionic acid and succinic acid are also reacted with nitro compounds to give the corresponding amide and imide (Table IV). From succinic acid, *N*-phenylsuccinimide was obtained. Employing nitroarenes having methyl, methoxyl, or chloro substituent, the corresponding amides were obtained in good yields.

Aliphatic nitro compounds can be employed as a substrate and similar reductive N-acylation proceeds to give the corresponding amides at 150 °C. The reaction proceeded at lower temperature with aliphatic nitro compounds as compared with nitroarenes, although the selectivity to the corresponding N-substituted amides was rather low.

Discussion

The possible reaction route for the present reaction is illustrated in Scheme I. In the reaction, a nitrene intermediate (1) would be generated from a nitro compound by deoxygenation with carbon monoxide (path a). The nitrene intermediate was also proposed in the transition-metal-catalyzed reaction of nitrobenzene with carbon monoxide.[11,12] The nitrene intermediate 1 in the present reaction seems unlikely as a free nitrene. The platinum-complexed nitrene (imido complex) might be more likely. Subsequently, the carbonylation of 1 to an isocyanate intermediate (2) seems to occur. Phenyl isocyanate was formed from phenyl azides under carbon monoxide pressure and/or in the presence of transition-metal catalyst.[13,14] There have been a number of studies in which Lewis acids promote a migratory insertion of carbon monoxide to a carbon–metal bond.[15] In the present reaction, the Lewis acid may be promoting the migratory insertion of carbon monoxide to a nitrene–metal bond, generating the isocyanate intermediate. We have previously proposed the aryl nitrene and phenyl isocyanate intermediate as key species in the platinum-catalyzed reductive N-carbonylation[16] and reduction[17] of nitroarenes. Several transition-metal nitrene[18] and isocyanate[19,20] organometallic complexes were isolated and characterized. The amide 4 is finally produced by the reaction of the isocyanate 2 with carboxylic acid followed by decarboxylation (path c). After the reaction (run 7), 3 times as much CO_2 as nitrobenzene by molar quantity is detected in the gas phase, which is consistent with the sequence of the reactions, paths a, b, and c.

Table V. Reductive N-Acylation of Nitrobenzene Catalyzed by Pt Complexes. Time-Course of the Reaction[a]

run	reactn time, h	convn,[b] %	yield,[b] %		material[c] balance, %
			acetanilide	aniline	
35	1	35	trace	9	26
36	2	90	41	24	72
7	4	100	91	0	91

[a] A mixture of nitrobenzene (10 mmol), acetic acid (40 mmol), $PtCl_2(PPh_3)_2$ (0.1 mmol), $SnCl_4$ (1.0 mmol), and dioxane (18 mL) was stirred at 180 °C under carbon monoxide of 60 atm. [b] Determined by GLC based on the amount of nitrobenzene charged. [c] 100 × [(yield of acetanilide + yield of aniline)]/convn.

Phenyl isocyanate reacted with acetic acid at 100 °C as a control experiment to give acetanilide in 87% yield with evolution of CO_2. This reaction was followed by GLC (Silicone OV-17, programmed from 100 °C to 160 °C by 5 °C/min). The reaction apparently showed only a poor material balance (less than 15%) according to the GLC analysis in the course of the reaction, whereas finally acetanilide was obtained in good yield after the reaction was completed. The reaction proceed via an intermediate which could not be detected by the GLC analysis. This intermediate is carbamic carboxylic anhydride, which is relatively unstable and cannot be isolated as a pure form.[21]

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Table VI. Reductive N-Acylation of Nitrobenzene Catalyzed by Pt Complexes. Effect of Acetic Acid/Nitrobenzene Ratio[a]

run	nitrobenzene, mmol	acetic acid/ nitrobenzene ratio	convn,[b] %	yield,[b] % acetanilide	yield,[b] % aniline
7	10	4.00	100	91	0
37	25	2.50	100	81	4
38	25	1.05	97	49	16
39[c]	25	1.05	99	51	10

[a] $PtCl_2(PPh_3)_2$, 1 mol % based on nitrobenzene; $SnCl_4$, 10 mol % based on nitrobenzene; dioxane (15–18 mL) at 180 °C for 4 h under carbon monoxide of 60 atm. [b] Determined by GLC based on the amount of the nitrobenzene charged. [c] For 10 h.

In the present study, we failed to detect the intermediate. The intermediate was successfully isolated by use of thiocarboxylic acid and phenyl isocyanate.[22]

As shown in Table V, material balance also was not good in the course of the catalytic reaction (runs 35 and 36), whereas after completion of the reaction the material balance reached 91%. This reaction features resemble those of phenyl isocyanate and acetic acid. In the reaction, carbamic carboxylic anhydride was derived from phenyl isocyanate (**2**), and this caused the low material balance observed in runs 35 and 36.

In Table V, aniline was detected in the reaction mixture after 1 and 2 h. This indicates that there exists another route to the amide via an amino intermediate (**3**) (path f). Aniline reacted with acetic acid in dioxane at 180 °C to give acetanilide in 54% yields. In the presence of the platinum catalyst system, a similar reaction produced acetanilide in 65% yield. Those yields, however, could not eventually exceed the yield of run 7. It is known that the synthesis of amides from carboxylic acid and amine succeeds poorly with less basic amine.[23]

There are two possibilities for the production of the amino compound **3**. One is from the isocyanate intermediate **2** and water via a carbamic acid derivative followed by decarboxylation to the amino compound **3** (path d). Water can be generated by a self-condensation of the carboxylic acid (eq 2). A small amount of water is sufficient for the paths d–f, since water is regenerated in path f. We have already reported the aminoarene formation from nitroarene under water gas shift reaction conditions in the presence of a similar platinum catalyst system (eq 3).[17] In that reaction, we also proposed phenyl isocyanate as a key intermediate to rationalize the chemoselectivity of the reaction. In Table I (run 9), the amount of aniline increases to 28% with addition of H_2O. This may be due to path d. The possible other route to amino compound **3** formation is direct hydrogen abstraction of nitrene intermediate **1** from the solvent or other hydrogen source[24] (path e). When the reaction was carried out by using acetic anhydride in place of acetic acid, the conversion of nitrobenzene was low and acetanilide was not obtained at all. This result indicates that the only possible hydrogen source is the carboxylic acid, even if the path e is operative. Table VI shows the effect of acetic acid/nitrobenzene ratio of the reaction. Acetanilide was obtained in 51% yield even if the ratio is 1.05. As mentioned above, 3 times as much CO_2 as nitrobenzene by molar quantity is generated. Carbon dioxide does not evolve in paths e and f. Therefore, the amount of evolved CO_2 should be reduced, if the reaction proceeds via paths e–f. Consequently, path e–f is not operating and amino compound **3** is most likely generated from path d.

$$2RCOOH \rightarrow (RCO)_2O + H_2O \qquad (2)$$

$$ArNO_2 + H_2O + 3CO \xrightarrow[80\ ^\circ C,\ 4\ h]{[Pt\text{-}Sn]} ArNH_2 + 3CO_2 \qquad (3)$$

We consider that the route via isocyanate (**2**), path a–b–c, is the predominant one. Kajimoto and Tsuji also concluded the same reaction route without any positive evidence. In the present reaction, a considerable amount of the amide (at least 24%; run 36 in Table V) was produced via amino intermediate **3** (path a–b–d–f).

Experimental Section

Materials. 1-Nitrohexane was prepared by the method of Gilbert.[25] Other substrates used were commercial materials. The nitro compounds, carboxylic acids, solvents (dioxane and benzene), and Lewis acids were purified by distillation under an Ar atmosphere or recrystallization. Carbon monoxide (>99.9%) was a commercial product and used without further purification. The platinum complexes, $PtCl_2(PPh_3)_2$[26a] and $PtCl_2(PhCN)_2$,[26b] were prepared according to procedures in the literature.

General Procedure. A 100-mL stainless steel autoclave (Nitto Koatsu; SUS 316) equipped with a magnetically driven stirrer was used in the reactions. A glass liner was set in the autoclave and the inside was heated by a heat gun (400 W) for 2 min. After cooling in Ar stream, solvent (dioxane or benzene; 18 mL), carboxylic acid (40 mmol), nitro compound (10 mmol), $PtCl_2(PPh_3)_2$ (79 mg, 0.1 mmol; 1 mol % based on nitro compound), and $SnCl_4$ (0.12 mL, 1.0 mmol) were charged in this order. After sealing and purging with three 30-atm pressurization–depressurization cycles of carbon monoxide, the reactor was pressured to 60 atm with carbon monoxide (at room temperature). Then the autoclave was heated to 180 °C in 20 min with stirring (500 rpm) and held at this temperature for 4 h. The reaction was terminated by rapid cooling, and gaseous product was discharged. The resulting brown solution was analyzed by GLC. In some reactions, all the gaseous product was collected in a gas buret and analyzed with GC.

Analytical Procedure. The identification of the products was confirmed by ^{13}C NMR, ^1H NMR, IR, and elemental analyses. The boiling points and melting points are uncorrected.

GLC analyses were performed on Shimadzu GC-4CM and GC-8A chromatographs with a column (3 mm i.d. × 3 m) packed with Silicone OV-17 (2% on Uniport HP, 60–80 mesh) programmed from 100 °C to 160 °C at 5 °C/min or a column (3 mm i.d. × 2.9 m) packed with PEG-HT (5% on Uniport HP, 60–80 mesh) programmed from 60 °C to 200 °C at 10 °C/min after 10 min at 60 °C. The gas phase was analyzed on a Shimadzu GC-3BT chromatograph with a column (3 mm i.d. × 3 m) packed with activated charcoal, 60–80 mesh, at 80 °C.

The ^1H NMR spectra were obtained at 100 MHz with a JEOL JNM FX-100 spectrometer, and ^{13}C NMR spectra were recorded at 25.05 MHz with a JEOL JNM FX-100 spectrometer, using tetramethylsilane as an internal standard, and samples were dissolved in $CDCl_3$ or Me_2SO-d_6. IR spectra were measured on a Hitachi Model 215 grating spectrophotometer. Elemental analyses were performed at the Microanalytical Center of Kyoto University. The analytical data of the products are described below. The phenyl carbon resonances in ^{13}C NMR spectra were tentatively assigned by calculating their chemical shifts with additive parameters.[27]

Acetanilide: light yellow crystals, Kugelrohr distillation (70–71 °C/0.5 mmHg; 1 mmHg = 133.322 Pa). All spectra data (^1H NMR, ^{13}C NMR, and IR spectra) were consistent with those of an authentic sample.

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***N*-(4-Methylphenyl)acetamide**: yellow crystals, Kugelrohr distillation (78–79 °C/0.6 mmHg); ^{1}H NMR (Me$_2$SO-d_6) δ 2.03 (s, 3 H, COCH$_3$), 2.23 (s, 3 H, CH$_3$) 3.43 (s, 1 H, -NH-), 7.03–7.53 (m, 4 H, phenyl); ^{13}C NMR (Me$_2$SO-d_6) 20.3 (q, CH$_3$), 23.8 (q, COCH$_3$), 118.9 (d, phenyl 2, 6), 128.8 (d, phenyl 3, 5), 131.6 (s, phenyl 4), 136.7 (s, phenyl 1), 167.8 (s, C=O); IR (KBr) 3300 cm^{-1} (ν_{NH}), 1660 cm^{-1} ($\nu_{C=O}$). Anal. Calcd for $C_9H_{11}NO$: C, 72.46; H, 7.43; N, 9.39; O, 10.72. Found: C, 72.26; H, 7.49; N, 9.41;, O, 10.61.

***N*-(4-Methoxyphenyl)acetamide**: white crystals, Kugelrohr distillation (84–89 °C/0.5 mmHg); ^{1}H NMR (CDCl$_3$) δ 2.10 (s, 3 H, COCH$_3$), 3.76 (s, 3 H, OCH$_3$), 6.76–7.42 (m, 4 H, phenyl), 7.94 (br, 1 H, -NH-); ^{13}C NMR (Me$_2$SO-d_6) 23.7 (q, COCH$_3$), 37.8 (q, OCH$_3$), 113.6 (d, phenyl 2, 6), 120.5 (d, phenyl 3, 5), 132.4 (s, phenyl 4), 154.9 (s, phenyl 1), 167.6 (s, C=O); IR (KBr) 3250 cm^{-1} (ν_{NH}), 1650 cm^{-1} ($\nu_{C=O}$). Anal. Calcd for $C_9H_{11}NO_2$: C, 65.44; H, 6.71; N, 8.48; O, 19.37. Found: C, 65.73; H, 6.55; N, 8.49; O, 19.53.

***N*-(4-Chlorophenyl)acetamide**: yellow crystals, Kugelrohr distillation (78–80 °C/0.5 mmHg); ^{1}H NMR (Me$_2$SO-d_6) δ 2.05 (s, 3 H, COCH$_3$), 3.38 (s, 1 H, -NH-), 7.22–7.66 (m, 4 H, phenyl); ^{13}C-NMR (Me$_2$SO-d_6) 23.9 (q, COCH$_3$), 120.4 (d, phenyl 2, 6), 126.5 (s, phenyl 4), 128.3 (d, phenyl 3, 5), 138.1 (s, phenyl 1), 168.2 (s, C=O); IR (KBr) 3300 cm^{-1} (ν_{NH}), 1660 cm^{-1} ($\nu_{C=O}$). Anal. Calcd for C_8H_8NOCl: C, 56.65; H, 4.75; N, 8.26; O, 9.43; Cl, 20.90. Found: C, 56.94; H, 4.65; N, 8.49; O, 9.52; Cl, 20.83.

***N*-Phenylpropanamide**: yellow crystals, Kugelrohr distillation (73–75 °C/0.3 mmHg); ^{1}H NMR (CDCl$_3$) δ 1.17 (t, 3 H, CH$_2$C*H*$_3$), 2.34 (q, 2 H, C*H*$_2$CH$_3$), 7.03–7.56 (m, 5 H, phenyl), 8.41 (br, 1 H, -N*H*-); ^{13}C NMR (Me$_2$SO-d_6) 9.6 (q, CH$_2$CH$_3$), 29.5 (t, COCH$_2$), 118.9 (d, phenyl 2, 6), 122.7 (d, phenyl 4), 128.4 (d, phenyl 3, 5), 139.1 (s, phenyl 1), 171.8 (s, C=O); IR (KBr) 3250 cm^{-1} (ν_{NH}), 1660 cm^{-1} ($\nu_{C=O}$). Anal. Calcd for $C_9H_{11}NO$: C, 72.46; H, 7.43; N, 9.39; O, 10.72. Found: C, 72.17; H, 7.21; N, 9.20; O, 10.88.

***N*-Phenylsuccinimide**: white crystals, sublimation under reduced pressure, mp 153–154 °C; ^{1}H NMR (Me$_2$SO-d_6) δ 2.77 (s, 4 H, -COC*H*$_2$C*H*$_2$CO-), 7.20–7.55 (m, 5 H, phenyl); ^{13}C NMR (CDCl$_3$) 28.4 (t, -CO*C*H$_2$*C*H$_2$CO-), 126.4 (d, phenyl 2, 6), 128.5 (d, phenyl 4), 129.1 (d, phenyl 3, 5), 176.1 (s, C=O); IR (KBr) 1700 cm^{-1} ($\nu_{C=O}$). Anal. Calcd for $C_{10}H_9NO_2$: C, 68.56; H, 5.18; N, 8.00; O, 18.27. Found: C, 68.39; H, 5.06; N, 7.99; O, 18.51.

***N*-Propylacetamide**: light yellow oil, Kugelrohr distillation (60–65 °C/2.0 mmHg); ^{1}H NMR (CDCl$_3$) δ 0.93 (t, 3 H, CH$_2$C*H*$_3$), 1.53 (m, 2 H, C*H*$_2$CH$_3$), 2.08 (s, 3 H, COCH$_3$), 3.20 (m, 2 H, -NHC*H*$_2$-), 8.02 (br, 1 H, -NH-); ^{13}C NMR (CDCl$_3$) 11.45 (q, CH$_3$), 22.31 (t, *C*H$_2$CH$_3$), 22.54 (q, COCH$_3$), 40.92 (t, -NHCH$_2$-), 169.96 (s, C=O); IR (neat) 3300 cm^{-1} (ν_{NH}), 1650 cm^{-1} ($\nu_{C=O}$).

Determination of CO$_2$ in the Gas Phase. An amount of CO$_2$ evolved was estimated with GC by the absolute calibration method. The calibration curve was obtained as follows. A mixture of benzene (18.0 mL), acetic acid (40 mmol), and SnCl$_4$ (1.0 mmol) was set in the 100-mL stainless steel autoclave. To this solution was added 366 mg (8.32 mmol), 716 mg (16.3 mmol), or 1294 mg (29.4 mmol) of dry ice (Seitetsu Kagaku; >99.8%), and immediately the autoclave was sealed. The autoclave was heated to 180 °C and held at this temperature for 1 h. After cooling, whole gas was collected in a gas buret and shaken to secure good homogeneity. One milliliter of the collected gas was subjected to GC 4 times and the absolute area of the chromatograph was measured.

Reaction of Aniline with Acetic Acid. To a 100-mL stainless steel autoclave were charged aniline (10 mmol), acetic acid (2.3 mL, 40 mmol), and solvent (benzene; 18 mL). The reaction was performed at 180 °C for 4 h with stirring (500 rpm). Acetanilide was obtained in 54% yield. The above reaction was performed in the presence of the platinum catalyst (0.1 mmol of PtCl$_2$(PPh$_3$)$_2$ and 1.0 mmol of SnCl$_4$). Acetanilide was obtained in 65% yield both Ar atmosphere or under CO pressure (initial 60 atm).

Reaction of Phenyl Isocyanate with Acetic Acid. A mixture of phenyl isocyanate (3.3 mmol), acetic acid (0.76 mL, 13.3 mmol), and dioxane (6.0 mL) was heated under reflux for 4 h. The GLC analysis indicated that almost all phenyl isocyanate was converted, and acetanilide was obtained in 87% yield. This reaction, however, did not proceed substantially at room temperature.

Reaction with Acetic Anhydride in Place of Acetic Acid. To a 100-mL stainless steel autoclave were charged dioxane (18 mL), acetic anhydride (20 mmol), nitrobenzene (10 mmol), PtCl$_2$(PPh$_3$)$_2$ (79.0 mg, 0.1 mmol), and SnCl$_4$ (0.12 mL, 1.0 mmol) in this order. The reaction was performed at 180 °C for 4 h under 60 atm of carbon monoxide pressure (initial). The GLC analysis of the resulting reaction solution indicated that the conversion of nitrobenzene was 18%, and acetanilide was not obtained in the reaction mixture.

Registry No. PtCl$_2$(PPh$_3$)$_2$, 10199-34-5; PtCl$_2$(PhCN)$_2$, 14873-63-3; PPh$_3$, 603-35-0; P(*o*-Tol)$_3$, 6163-58-2; PBu$_3$, 998-40-3; Ph$_2$P(CH$_2$)$_2$PPh$_2$, 1663-45-2; SnCl$_4$, 7646-78-8; SnCl$_2$, 7772-99-8; FeCl$_3$, 7705-08-0; VCl$_3$, 7718-98-1; AlCl$_3$, 7446-70-0; ZnCl$_2$, 7646-85-7; PhNO$_2$, 98-95-3; NO$_2$-*p*-C$_6$H$_4$CH$_3$, 99-99-0; NO$_2$-*p*-C$_6$H$_4$Cl, 100-00-5; NO$_2$-*p*-C$_6$H$_4$OMe, 100-17-4; CH$_3$(CH$_2$)$_2$NO$_2$, 108-03-2; CH$_3$(CH$_2$)$_5$NO$_2$, 646-14-0; CH$_3$C(O)NH(CH$_2$)$_5$CH$_3$, 7501-79-3; CH$_3$CH$_2$CO$_2$H, 79-09-4; HO$_2$C(CH$_2$)$_2$CO$_2$H, 110-15-6; CH$_3$CO$_2$H, 64-19-7; CH$_3$CH$_2$C(O)NHPh, 620-71-3; CH$_3$C(O)NH-*p*-C$_6$H$_4$CH$_3$, 103-89-9; CH$_3$C(O)NH-*p*-C$_6$H$_4$Cl, 539-03-7; CH$_3$C(O)NH-*p*-C$_6$H$_4$OMe, 51-66-1; CH$_3$C(O)NHPr, 5331-48-6; CO, 630-08-0; PhNH$_2$, 62-53-3; PhNCO, 103-71-9; *N*-phenylsuccinimide, 83-25-0.