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Preparation of Acyl(carboxylato)bis(tertiary phosphine)palladium(II) Complexes by C–O Bond Cleavage of Carboxylic Anhydrides on Interaction with Palladium(0) Complexes. Catalytic Hydrogenation of Carboxylic Anhydrides to Aldehydes by Palladium Complexes

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Acyclic anhydrides oxidatively added to [Pd(styrene)($PMeR_2$)$_2$] (R = Me, **2a**; Ph, **2b**) under mild conditions with C–O bond cleavage to give the corresponding *trans*-acyl(carboxylato)palladium complexes **3a**—**3h**. Cyclic acid anhydrides also added to **2a** to yield *trans*-acyl(carboxylato)palladium complexes **4a**—**4c**, while reaction of **2a** with phthalic anhydride afforded the palladalactone **4d** generated via oxidative addition followed by decarbonylation. The acetyl(acetato)palladium complex **3a** reacted with dihydrogen or formic acid to give acetaldehyde and acetic acid. Catalytic hydrogenation of acyclic anhydrides by a palladium complex was achieved to form the corresponding aldehydes and carboxylic acids.

Oxidative addition of organic halides to low valent transition metal complexes provides useful means to prepare reactive organotransition metal halides.[1] Combination of the process with other elementary processes such as transmetallation, olefin and CO insertion into metal–carbon bond, and reductive elimination have afforded a variety of synthetically useful processes catalyzed by transition metal complexes. An intrinsic problem with the processes utilizing organic halides as substrates is the necessity of removing the halides with stoichiometric amounts of a base with formation of salts of hydrogen halides for preparing products containing no halides. Thus these processes do not have high total efficiency and are not considered environmentally benign.

For synthesizing oxygen-containing organic compounds, we expect the utilization of processes involving carbon–oxygen bond cleavage of organic compounds promoted by transition metal complexes are expected to provide useful methodology in organic synthesis, a way which needs no process to remove the halides. However, except for processes involving cleavage of allylic oxygen bond, relatively few processes involving C–O bond cleavage have been examined and their application to organic synthesis still remains mostly unexplored.[2] Carbonyl-containing compounds, particularly those having electron-withdrawing groups, are expected to interact with low-valent transition metal complexes to undergo oxidative addition reactions to give acyltransition metal complexes. In fact, stoichiometric oxidative addition of some carbonyl compounds has been observed and their synthetic applications involving the C–O bond activation have been reported.[3] Reactions of electron-rich nickel(0) complexes with electron-deficient carboxylic esters[4] and anhydrides[5] have been studied to reveal the ease of acyl–oxygen bond cleavage. One difficulty of using the nickel-promoted C–O bond cleavage is the occurrence of decarbonylation of acyl–nickel bond, affording nickel carbonyl compounds that are less reactive and resist further utilization for catalytic processes. Corresponding palladium complexes, on the other hand, are expected to have less affinity toward CO and to provide a better chance of realizing catalytic processes under mild conditions. We have previously reported in a communication that carboxylic anhydrides oxidatively add to palladium(0) complexes.[6,7] The present paper is concerned with a more detailed description of the oxidative addition of the anhydrides to Pd(0) complexes and with the results of examination of their chemical properties.[8] Application of the information obtained regarding reactivity of the resultant acyl(carboxylato)palladium(II) complexes to catalytic hydrogenation of the anhydrides to aldehydes is also reported.

Results and Discussion

Oxidative Addition of Acyclic Acid Anhydrides to Palladium(0) Complexes. Our previous studies showed that Pd(0) complexes prepared by thermolysis of [$PdEt_2(PR_3)_2$][9] in the presence of an olefin such as styrene or methyl acrylate yielded coordinatively unsaturated, reactive olefin-coordinated Pd(0) complexes suitable for further reactions with various compounds.[10] The styrene-coordinated Pd(0) complexes coordinated with PMe_3 and $PMePh_2$ ligands were found to readily react with various acyclic acid anhydrides at room temperature with C–O bond cleavage to give acyl(carboxylato)palladium(II) complexes

(Scheme 1).[11]

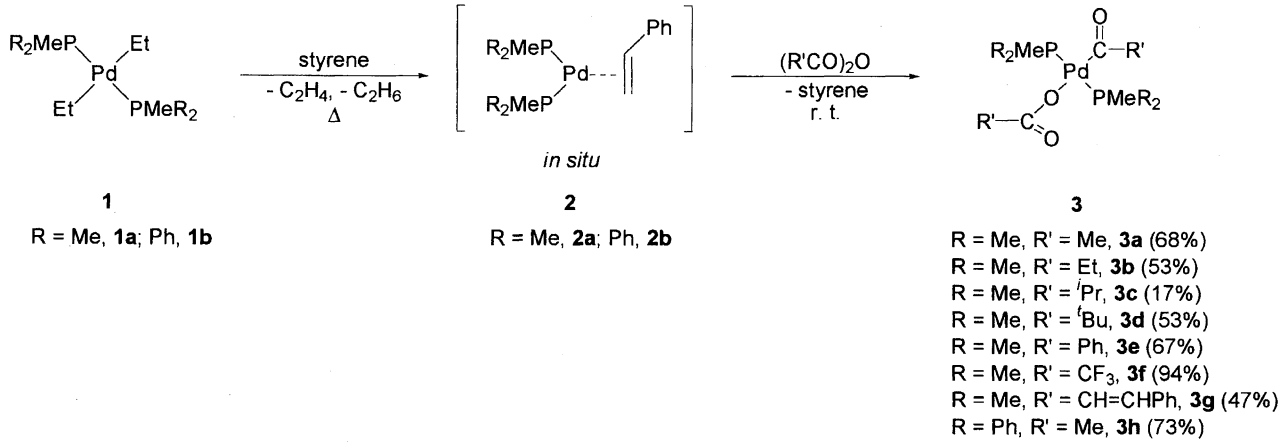
The acyl(carboxylato)palladium complexes have been characterized with spectroscopic methods and by elemental analysis. Particularly diagnostic data to support the *trans* configuration of the products were obtained from ^{1}H and ^{13}C{^{1}H} NMR signals of the methyl groups in the coordinated PMe_3 and $PMePh_2$ ligands observed as virtual triplets. Further, ^{31}P{^{1}H} NMR spectra of these compounds showed a singlet. The IR spectra of the acetato complexes support the coordination of the carboxylato ligand through a monodentate fashion. Scheme 2 shows the reactions of PMe_3-coordinated acetyl(acetato)palladium complex **3a** with various reagents.

Acetic acid did not protonate the acetyl ligand in **3a** to release acetaldehyde at room temperature. Each addition of increasing amounts of acetic acid to **3a** at room temperature caused the shift of the ^{1}H NMR acetato signal from δ = 1.69 to lower field (see Experimental section). The results suggest that the exchange of the coordinated acetato ligand with acetic acid takes place at room temperature. Similarly, the chemical shift change of the acetato ligand to lower field[12] was observed with ^{1}H NMR at −30 °C on each addition of increasing amounts of formic acid (see Experimental section).

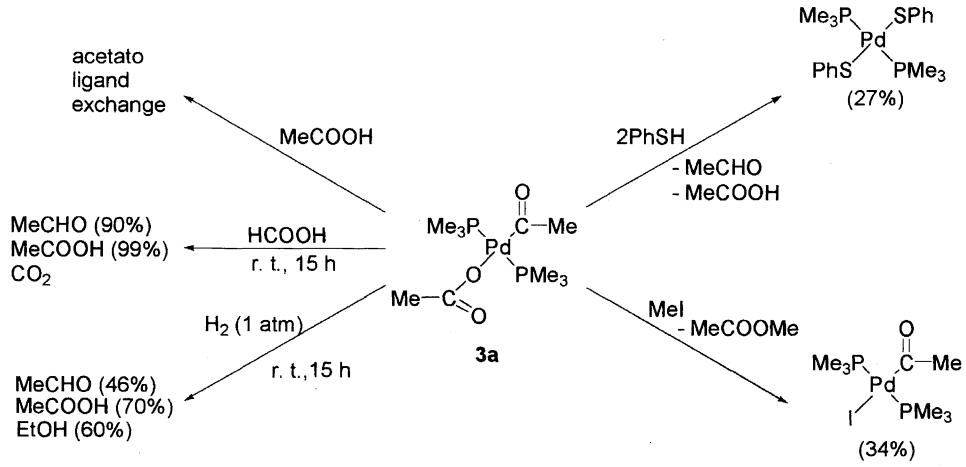
These results suggest the occurrence of fast exchange between the acetato ligand in **3a** with the added carboxylic acids. When **3a** was treated with 1 mol amt. of formic acid for 15 h at room temperature, decomposition of **3a** occurred to give a black precipitate of palladium with formation of 1 mol amt. each of acetaldehyde (90%) and acetic acid (99%).[13] The reaction was accompanied by formation of carbon dioxide, as confirmed by gas chromatography. These results indicate that the acetato ligand in **3a** exchanges with formic acid to give an acetyl(formato)palladium intermediate, which is decarboxylated to give an unstable acetyl(hydrido)palladium that liberates acetaldehyde on reductive elimination (Scheme 3).

Complex **3a** reacted at room temperature with two mol amt. of PhSH to yield [*trans*-Pd$(PMe_3)_2(SPh)_2$][14] with release of acetaldehyde and acetic acid, as confirmed by GC.

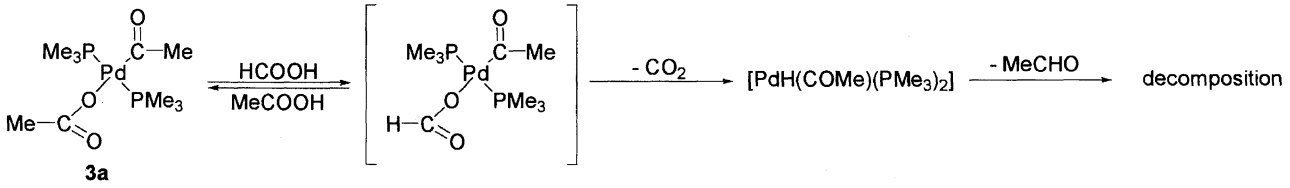
The reaction of **3a** with MeI, on the other hand, gave [*trans*-Pd(acetyl)I$(PMe_3)_2$] in a 34% yield with formation of methyl acetate as confirmed by GC. No formation of acetyl iodide or acetone was observed. The results imply that the electrophilic attack of the methyl group in MeI on the acetato ligand occurred without giving the oxidative addition product of **3a** with MeI. The acetylpalladium iodide complex was previously prepared by Werner.[15]



Scheme 1. Oxidative addition of acid anhydrides to Pd(0) complexes.



Scheme 2. Reactions of complex **3a**.



Scheme 3. Reaction **3a** with formic acid.

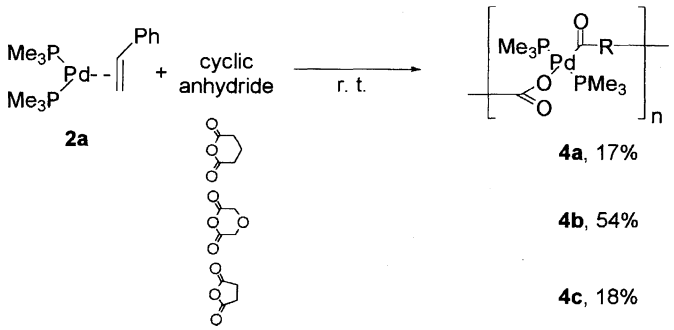
An interesting property of the acetyl(acetato)palladium complexes is its behavior towards dihydrogen. The reaction of complex **3a** with H_2 of atmospheric pressure at room temperature for 15 h liberated acetaldehyde (46%), acetic acid (70%), and ethanol (60%).[16] Aldehyde formation in the reaction of benzoylpalladium complex with H_2 has been reported by Heaton et al.[17]

Oxidative Addition of Cyclic Acid Anhydrides. Aliphatic cyclic acid anhydrides also add oxidatively to [Pd(styrene)(PMe_3)$_2$], **2a**, at room temperature to afford acyl(carboxylato)palladium complexes **4a**—**4c** having two PMe_3 ligands, as shown in Scheme 4.

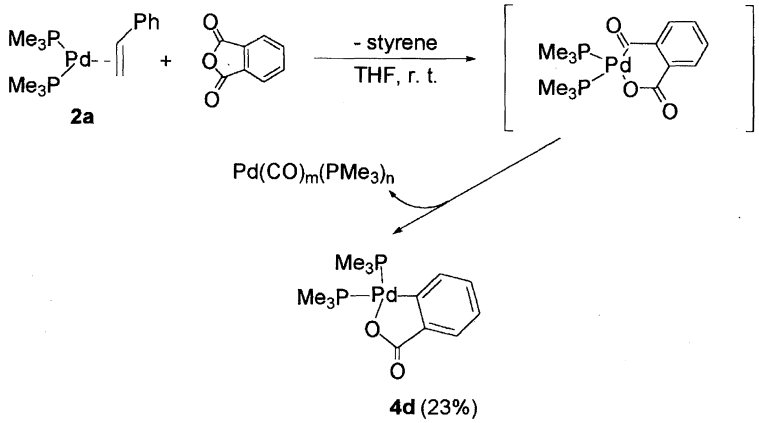
The ^1H and $^{13}C\{^1H\}$ NMR spectra of the complexes obtained show virtual triplets of the coordinated PMe_3 ligands supporting the trans configurations. $^{31}P\{^1H\}$ NMR also shows singlets in agreement with the trans configurations. Although complexes **4a**—**4c** are quite soluble in water, and show considerable solubilities in chlorine-containing solvents such as CD_2Cl_2 and $CDCl_3$, the solution is accompanied by a slow decomposition. They are poorly soluble in hydrocarbon solvents such as benzene, precluding an attempt of molecular weight determination by cryoscopic means. Oligomeric structures are tentatively assumed for these complexes.

Phthalic anhydride, a cyclic aromatic anhydride, was found to react with the Pd(0) complex differently. In the reaction of phthalic anhydride with **2a** in THF for 24 h at room temperature, the color of the reaction mixture gradually changed from yellow to deep red and white powder was precipitated from the reaction mixture (Scheme 5).

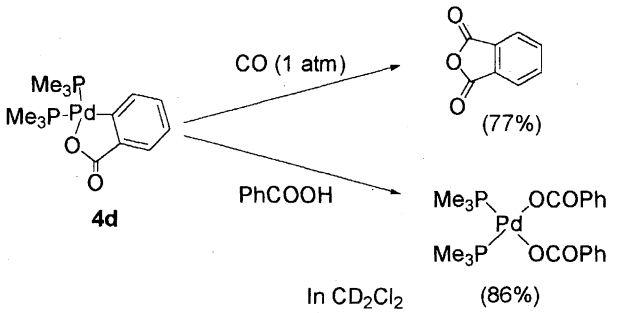
Characterization of the white solid by NMR and elemental analysis revealed that it is a palladalactone type complex **4d** (Scheme 6).[18] The $^{31}P\{^1H\}$ NMR showed the AB quartet at $\delta = -17.3$ and -3.37 ($^2J_{PP} = 41$ Hz). The $^{13}C\{^1H\}$ NMR showed a doublet of an aromatic carbon at $\delta = 157$ with a J_{PC} coupling constant of 124 Hz. The signal can be assigned to the *ipso* carbon of the palladalactone ring, with the metallated carbon situated at the site trans to one of the PMe_3 ligands. Examination of the reaction of **2a** with phthalic anhydride at room temperature with IR spectroscopy in THF revealed the



Scheme 4. Oxidative addition of cyclic acid anhydrides to **2a**.



Scheme 5. Oxidative addition of phthalic anhydride to **2a**.



Scheme 6. Reactions of complex **4d**.

gradual growth of a band at 1936 cm^{-1} in several days. Since the reaction of [Pd(styrene)(PMe_3)$_2$] with CO gives a CO-coordinated complex with the ν_{CO} band at 1937 cm^{-1}, the absorption at 1936 cm^{-1} is ascribed to the palladium-bound CO arising from a palladium–carbonyl complex formed in the reaction. Formation of the CO-coordinated Pd(0) complex accounts for the low yield of the palladalactone complex **4d**. Treatment of the palladalactone **4d** with 1 atm of CO liberated phthalic anhydride in 77% yield.[19] The result suggests the CO insertion into the Pd–C bond in the palladacycle to give a cyclic acyl(carboxylato)palladium type intermediate that undergoes the reductive elimination to afford the phthalic anhydride. As further support of the palladalactone structure, treatment of **4d** with 1 mol amt. of benzoic acid afforded [*cis*-Pd(OCOPh)$_2$(PMe_3)$_2$] in 86% yield. We have previously found that the *cis*-dibenzoato complex can be prepared by an independent route by the reaction of [Pd(methyl acrylate)-(PMe_3)$_2$] with benzoyl peroxide.[20]

Hydrogenation of Acid Anhydrides Catalyzed by a Palladium Complex. The finding that the acyl(carboxylato)palladium complex **3a** reacted with dihydrogen to release aldehyde and acid suggested the possibility of realizing the catalytic hydrogenation of anhydrides with a palladium complex.[21] In fact, by heating mixtures of anhydrides and [$Pd(PPh_3)_4$] (0.01 mol amt. of the anhydride) in THF at 80 °C under 3.0 MPa of dihydrogen, aldehydes, and carboxylic acids were produced in excellent yields with octanoic anhydride and benzoic anhydride (Table 1).

Cinnamic anhydride also can be converted into cinnamaldehyde and cinnamic acid in moderate yields. Formation of styrene (17%) and a trace of ethylbenzene was confirmed, suggesting occurrence of decarbonylation from cinnamoyl ligand bound to palladium to give β-styrylpalladium species that is hydrogenated. Another type of aliphatic unsaturated anhydride, oleic anhydride, reacted with dihydrogen in the presence of the Pd(0) complex to give its corresponding aldehyde and carboxylic acid in good yields. A more hindered anhydride, isobutyric anhydride, was hydrogenated in moderate yield, whereas the catalytic reaction of pivalic (trimethylacetic) anhydride with H_2 proceeded sluggishly to give the corresponding aldehyde in a minor amount, while most of the starting anhydride remained unreacted after 24 h.

Conclusion

Oxidative addition of acid anhydrides with Pd(0) complexes was found to proceed readily to yield acyl(carboxylato)palladium type complexes. The palladium complexes are less prone to decarbonylation than the corresponding nickel analogs, which form less reactive CO-coordinated complexes. On the basis of the chemistry of the acyl(carboxylato)palladium complexes with dihydrogen, a novel catalytic hydrogenation of anhydrides to aldehydes and carboxylic acids was discovered. The catalytic hydrogenation of anhydrides to aldehydes and carboxylic acids may provide useful routes to certain aldehydes from some anhydrides. The process has some advantage over the classical Rosenmund processes using acyl chlorides in that usage of acid chlorides and a base to remove hydrogen chloride is not required. We later found that a direct catalytic conversion of carboxylic acids into aldehydes can be achieved under certain conditions. The process will be the subject of a separate report.[22]

$$\underset{2\ \text{mmol}}{(RCO)_2O} + \underset{3.0\ \text{MPa}}{H_2} \xrightarrow[\text{THF, 80 °C, 24 h}]{[Pd(PPh_3)_4]\ 0.02\ \text{mmol}} RCHO + RCOOH$$

Table 1. Catalytic Hydrogenation of Acyclic Acid Anhydrides

Entry	R	Yield[a]/%		
		RCHO	RCOOH	Other products
1	$^nC_7H_{15}$	97	99	
2	C_6H_5	99	97	
3	*trans*-PhCH=CH[b]	53	81	Ph⟋⟍ 17 Ph⟋ tr.
4	*cis*-C_8H_{17}CH=CHC_7H_{14}	74[c]	90[c]	
5	$(CH_3)_2CH$	67[d]	75	(^{i}PrCO)$_2$O 21% remained
6	$(CH_3)_3C$	11[d]	24	(^{t}BuCO)$_2$O 82% remained

a) Determined by GC unless otherwise noted. b) Reaction time, 96 h. c) Isolated yields. d) Determined by ^{1}H NMR.

Experimental

All manipulations were carried out under argon using Schlenk tube technique. Solvents were purified by usual methods under argon. Palladium(II) dichloride was purchased from Tanaka-Kikinzoku Co. and used without purification. All anhydrides except *trans*-cinnamic anhydride[23] were commercial products and used without further purification. NMR data were obtained on Hitachi R-90H, JEOL EX-270, or JEOL GSX-400 using acetone-d_6 as solvent unless otherwise noted. The chemical shifts in $^{31}P\{^1H\}$ NMR are in ppm from external 85%-H_3PO_4. The multiplicity applied to the PMe_3 and $PMePh_2$ resonances in ^1H and $^{13}C\{^1H\}$ NMR, refer to apparent splitting patterns and the values reported as coupling constants for these resonances are the separation between the peaks and do not reflect the true coupling constants. IR spectra were obtained on Hitachi I-3000 or Perkin Elmer Paragon 1000. Gas chromatography was carried out on a Hitachi 263-50 equipped with 5%-SE30 or GasukuroPACK 54. Low-resolution mass spectra combined with gas chromatograph results were obtained with Shimadzu QP-1000 and JEOL JMS-SX102A.

Preparation of *trans*-Acyl(carboxylato)[bis(tertiary phosphine)]palladium(II) 3a—3h. These acyl(carboxylato)palladium complexes were prepared in a similar manner. As one example, preparation of **3a** is described below. The other physical data, NMR, and IR data as well as the results of elemental analysis are also given.

3a: An acetone solution (7.3 cm^3) of $[PdEt_2(PMe_3)_2]$[9] (1.16 g, 3.65 mmol) and styrene (0.85 cm^3, 7.4 mmol) was heated at 50 °C for 50 min. After cooling the solution at room temperature, we added acetic anhydride (0.34 cm^3, 3.6 mmol) to the solution, which was allowed to stand for 30 min at room temperature. A white solid was obtained by removing acetone and styrene in vacuo and the residue was recrystallized from Et_2O to give white needles, which were washed with hexane repeatedly. White needles of **3a** were obtained in 68% yield (894 mg). ^1H NMR (90 MHz) δ = 1.30 (t, 18H, J = 3.74 Hz, virtual coupling, P*Me*$_3$), 1.70 (s, 3H, C*H*$_3$COO), 2.28 (br. s, 3H, C*H*$_3$CO); $^{13}C\{^1H\}$ NMR (100.5 MHz) δ = 14.2 (br. s, P*Me*$_3$), 24.9 (s, CH_3COO), 41.5—42.5 (m, *C*H$_3$CO), 175.9 (s, CH_3COO), 237.2 (s, CH_3CO); $^{31}P\{^1H\}$ NMR (161.8 MHz) δ = −19.2 (s); IR 1676 ($\nu_{C=O}$), 1572 (ν_{COO}), 956 cm^{-1} (ν_{P-C}). Found: C, 33.41, H, 7.10%. Calcd for $C_{10}H_{24}O_3P_2Pd$: C, 33.30, H, 6.71%. Mp 69—71 °C (decomp).

3b: White powder (53%). ^1H NMR (90 MHz): δ = 0.88 (t, 3H, $^2J_{HH}$ = 7.91 Hz, C*H*$_3$CH$_2$COO), 0.91 (t, 3H, $^2J_{HH}$ = 7.48 Hz, C*H*$_3$CH$_2$CO), 1.28 (t, 18H, J = 3.74 Hz, virtual coupling, P*Me*$_3$), 1.96 (q, 2H, $^2J_{HH}$ = 7.91 Hz, CH$_3$C*H*$_2$COO), 2.58 (q, 2H, $^2J_{HH}$ = 7.48 Hz, CH$_3$C*H*$_2$CO); $^{13}C\{^1H\}$ NMR (100.5 MHz) δ = 9.5 (s, C*H*$_3$CH$_2$COO), 12.0 (s, *C*H$_3$CH$_2$CO), 14.5 (br. s, P*Me*$_3$), 31.2 (s, CH$_3$*C*H$_2$COO), 49.2 (s, CH$_3$*C*H$_2$CO), 179.0 (s, CH$_3$CH$_2$*C*OO), 239.6 (s, CH$_3$CH$_2$*C*O); $^{31}P\{^1H\}$ NMR (161.8 MHz) δ = −23.5 (s); IR 1662 ($\nu_{C=O}$), 1566 (ν_{COO}), 956 cm^{-1} (ν_{P-C}). Found: C, 37.23, H, 7.80%. Calcd for $C_{12}H_{28}O_3P_2Pd$: C, 37.08, H, 7.26%. Mp 75—78 °C (decomp).

3c: White powder (17%). ^1H NMR (400 MHz) δ = 1.00 (d, 6H, $^2J_{HH}$ = 7.34 Hz, (C*H*$_3$)$_2$CHCOO), 1.24 (d, 6H, $^2J_{HH}$ = 7.34 Hz, (C*H*$_3$)$_2$CHCO), 1.28 (t, 18H, J = 3.67 Hz, virtual coupling, P*Me*$_3$), 2.18—2.29 (m, 2H, (CH$_3$)$_2$*C*HCO and (CH$_3$)$_2$*C*HCOO); $^{13}C\{^1H\}$ NMR (67.9 MHz) δ = 14.8 (t, J = 13.3 Hz, virtual coupling, P*Me*$_3$), 19.3 (s, (*C*H$_3$)$_2$CHCOO), 21.5 (s, (*C*H$_3$)$_2$CHCO), 37.9 (s, (CH$_3$)$_2$*C*HCOO), 52.7 (s, (CH$_3$)$_2$*C*HCOO), 181.9 (s, (CH$_3$)$_2$CH*C*OO), 243.3 (s, (CH$_3$)$_2$CH*C*O); $^{31}P\{^1H\}$ NMR (109.4 MHz) δ = −13.6 (s); IR 1650 ($\nu_{C=O}$), 1546 (ν_{COO}), 954 cm^{-1} (ν_{P-C}). Found: C, 40.39, H, 8.13%. Calcd for $C_{14}H_{32}O_3P_2Pd$: C, 40.35, H, 7.74%. Mp 76—79 °C (decomp).

3d: White powder (53%). ^1H NMR (90 MHz) δ = 1.06 (s, 9H, (*CH*$_3$)$_3$CCOO), 1.17 (s, 9H, (*CH*$_3$)$_3$CCO), 1.31 (t, 18H, J = 3.96 Hz, virtual coupling, P*Me*$_3$); $^{13}C\{^1H\}$ NMR (67.9 MHz, $CDCl_3$, −20 °C) δ = 14.7 (t, J = 13.1 Hz, virtual coupling, P*Me*$_3$), 27.5 (s, (*CH*$_3$)$_3$CCOO), 28.6 (s, (*CH*$_3$)$_3$CCO), 39.7 (s, (CH$_3$)$_3$*C*COO), 53.9 (t, $^3J_{PC}$ = 11.8 Hz, (CH$_3$)$_3$*C*CO), 183.8 (s, (CH$_3$)$_3$*C*COO), 249.7 (s, (CH$_3$)$_3$*C*CO); $^{31}P\{^1H\}$ NMR (109.4 MHz) δ = −14.6 (s); IR 1644 ($\nu_{C=O}$), 1546 (ν_{COO}), 954 cm^{-1} (ν_{P-C}). Found: C, 43.55, H, 8.61%. Calcd for $C_{16}H_{36}O_3P_2Pd$: C, 43.20, H, 8.16%. Mp 104—106 °C (decomp).

3e: Yellow powder (67%). ^1H NMR (90 MHz) δ = 1.17 (t, 18H, J = 3.74 Hz, virtual coupling, P*Me*$_3$), 7.25—7.42 (m, 3H, aromatic H), 7.46—7.64 (m, 3H, aromatic H), 7.90—8.12 (m, 2H, aromatic H), 8.16—8.35 (m, 2H, aromatic H); $^{13}C\{^1H\}$ NMR (100.5 MHz) δ = 13.9 (t, J = 13.9 Hz, virtual coupling, P*Me*$_3$), 128.7 (s), 129.8 (s), 130.4 (s), 130.6 (s), 130.7 (s), 133.2 (s), 140.0 (s), 143.7 (s, aromatic C), 172.0 (s, Ph*C*OO), 233.3 (s, Ph*C*O); $^{31}P\{^1H\}$ NMR (109.4 MHz) δ = −19.3 (s); IR 1638 ($\nu_{C=O}$), 1558 (ν_{COO}), 952 cm^{-1} (ν_{P-C}). Found: C, 49.55, H, 5.82%. Calcd for $C_{20}H_{28}O_3P_2Pd$: C, 49.52, H, 5.92%. Mp 123—125 °C (decomp).

3f: White powder (94%). ^1H NMR (400 MHz, −10 °C) δ = 1.36 (t, 18H, J = 4.04 Hz, virtual coupling, P*Me*$_3$); $^{13}C\{^1H\}$ NMR (101 MHz) δ = 13.3 (t, J = 15.0 Hz, virtual coupling, P*Me*$_3$), 114.2 (tq, $^1J_{FC}$ = 298.8 Hz, $^3J_{PC}$ = 13.2 Hz, *C*F$_3$CO), 117.6 (q, $^1J_{FC}$ = 291.5 Hz, *C*F$_3$COO), 161.7 (q, $^2J_{FC}$ = 35.0 Hz, CF$_3$*C*OO), 222.7 (tq, $^2J_{FC}$ = 37.4 Hz, $^2J_{PC}$ = 3.67 Hz, CF$_3$*C*O); ^{19}F NMR (CD_2Cl_2, −30 °C, CF_3COOH as an external standard) δ = −75.0 (s, C*F*$_3$COO), −77.3 (s, C*F*$_3$CO); $^{31}P\{^1H\}$ NMR (109.4 MHz) δ = −16.8 (s); IR 1694 ($\nu_{C=O}$), 1430 (ν_{COO}), 948 cm^{-1} (ν_{P-C}). Found: C, 25.86, H, 4.02%. Calcd for $C_{10}H_{18}F_6O_3P_2Pd$: C, 25.63, H, 3.87%. Mp 71.5—73.0 °C (under Ar, decomp).

3g: Yellow powder (47%). ^1H NMR (270 MHz, CD_2Cl_2) δ = 1.26 (t, 18H, J = 3.67 Hz, virtual coupling, P*Me*$_3$), 6.32 (dt, 1H, $^3J_{HH}$ = 16.1 Hz, $^4J_{PH}$ = 0.92 Hz, PdC(=O)C*H*=CHPh), 6.51 (d, 1H, $^3J_{HH}$ = 15.8 Hz, PdOC(=O)C*H*=CHPh), 7.33 (d, 1H, $^3J_{HH}$ = 15.8 Hz, PdOC(=O)CH=C*H*Ph), 7.24—7.38 (m, 3H), 7.40—7.46 (m, 3H), 7.48—7.55 (m, 2H, aromatic H), 7.62—7.69 (m, 2H, aromatic H), 8.28 (d, $^3J_{HH}$ = 16.1 Hz, PdC(=O)CH=C*H*Ph); $^{13}C\{^1H\}$ NMR (67.9 MHz) δ = 13.7 (t, J = 13.9 Hz, virtual coupling, P*Me*$_3$), 127.7 (s), 128.5 (s), 129.3 (s), 129.7 (s), 129.9 (s), 130.3 (s), 131.3 (s), 134.2 (t, $^3J_{PC}$ = 13.5 Hz, PhCH=*C*HCOPd), 136.5 (s), 137.4 (s), 139.1 (s), 151.9 (s, aromatic C and C=C), 172.4 (s, PhCH=CH*C*OO), 233.9 (s, PhCH=CH*C*OPd); $^{31}P\{^1H\}$ NMR (109.4 MHz) δ = −18.5 (s); IR 1622 ($\nu_{C=O}$), 1578 (ν_{COO}), 948 cm^{-1} (ν_{P-C}). Found: C, 54.05, H, 5.53%. Calcd for $C_{24}H_{32}O_3P_2Pd$: C, 53.69, H, 6.01%. Mp 120—121 °C (decomp).

3h: White powder (73%). ^1H NMR (400 MHz, CD_2Cl_2, −20 °C) δ = 1.37 (s, 3H, C*H*$_3$COO), 1.41 (br. s, 3H, C*H*$_3$CO), 1.90 (t, 6H, J = 3.49 Hz, virtual coupling, PPh$_2$*Me*), 7.40—7.50 (m, 12H, P*Ph*$_2$Me), 7.60—7.80 (m, 8H, P*Ph*$_2$M); $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, −20 °C) δ = 11.6 (t, J = 13.1 Hz, virtual coupling, PPh$_2$*Me*), 23.8—24.1 (m, *C*H$_3$COO), 37.5—39.1 (m, *C*H$_3$CO), 125.0 (s), 128.6 (t, J = 4.77 Hz, virtual coupling), 130.1 (s), 132.8 (s, P*Ph*$_2$Me), 176.2 (s, CH$_3$*C*OO), 237.2 (s, CH$_3$*C*O); $^{31}P\{^1H\}$ NMR (109.4 MHz, CD_2Cl_2, −20 °C) δ = 3.35 (s); IR 1650 ($\nu_{C=O}$), 1571 (ν_{COO}), 888 cm^{-1} (ν_{P-C}). Found: C, 59.60, H, 5.58%. Calcd for $C_{30}H_{32}O_3P_2Pd$: C, 59.17, H, 5.30%. Mp 80—81 °C (decomp).

Reaction of 3a with Acetic Acid. The ^1H NMR (90 MHz) spectrum of the solution of **3a** (5.4 mg, 0.015 mmol) in acetone-d_6

(0.5 cm^3) in an NMR tube was observed at room temperature after each addition of measured quantities of acetic acid. The amounts of acetic acid for each addition were as follows (total molar amounts of acetic acid per mol of **3a** in parentheses), 0 (0), 0.5 (0.58), 0.4 (1.0), 0.8 (2.0), 1.7 (4.0), 3.5 (8.0), 6.8 (16.0)$\times 10^{-3}$ cm^3. The chemical shift of the acetato signal of **3a** was shifted upon addition of acetic acid towards lower magnetic field: δ = 1.69 (0), 1.83 (0.58), 1.86 (1.0), 1.89 (2.0), 1.92 (4.0), 1.94 (8.0), 1.95 (16.0), 1.95 (free acetic acid).

Reaction of 3a with Formic Acid Observed with ^{1}H NMR The ^{1}H NMR (90 MHz) spectrum of the solution of **3a** (26.7 mg, 0.0740 mmol) in acetone-d_6 (0.5 cm^3) in an NMR tube was observed at −30 °C after each addition of measured amounts of additional formic acid. The amounts of formic acid for each addition were as follows (total molar amounts of formic acid per mol of **3a** in parentheses): 0 (0), 1.7 (0.6), 1.7 (1.2), 3.4 (2.4), 6.8 (4.9), 13.7 (10.2)$\times 10^{-3}$ cm^3. The chemical shifts of the acetato signal of **3a** and formic acid were shifted upon addition of formic acid towards lower and higher magnetic fields, respectively: δ = 1.68 (0); 1.84 (acetato), 8.28 (formyl hydrogen of formic acid) (0.6); 1.91, 8.29 (1.2); 1.94, 8.25 (2.4); 1.95, 8.20 (4.9); 1.96, 8.16 (10.2), 1.95, 8.12 (free acetic acid and free formic acid).

Reaction of 3a with Formic Acid. To an acetone solution (1 cm^3) of **3a** (53 mg, 0.15 mmol), formic acid (0.0056 cm^3, 0.14 mmol) was added at −50 °C and the solution was stirred at room temperature. After 15 h the solution was chilled to −70 °C; GC and GC-MS analyses were carried out with hexane as an internal standard. Acetic acid (99%), acetaldehyde (90%), and CO_2 were detected.

CH_3COOH Found: *m/z* 60 (M), 45 (M − CH_3), 43 (M − OH); CH_3CHO Found: *m/z* 44 (M), 43 (M − H), 29 (M − CH_3).

Reaction of 3a with Dihydrogen. Dihydrogen was introduced under atmospheric pressure into a colorless acetone solution (1 cm^3) of **3a** (40 mg, 0.11 mmol) at −70 °C. The solution gradually turned yellow on stirring at room temperature. After 15 h the yellow solution was chilled to −70 °C and GC and GC-MS analyses were performed with hexane as an internal standard. Formation of acetic acid (70%), acetaldehyde (46%), and ethanol (60%) was confirmed.

CH_3COOH Found: *m/z* 60 (M), 45 (M − CH_3), 43 (M − OH); CH_3CHO Found: *m/z* 44 (M), 43 (M − H), 29 (M − CH_3); CH_3CH_2OH Found: *m/z* 46 (M), 45 (M − H), 31 (M − CH_3).

Reaction of 3a with PhSH. To an acetone solution (2 cm^3) of **3a** (65 mg, 0.18 mmol), PhSH (0.0037 cm^3, 0.36 mmol) was added and the solution was stirred for 1.5 h at room temperature. A yellow precipitate was formed as the reaction proceeded. Formation of acetic acid (*m/z* 60) and acetaldehyde (*m/z* 44) was observed in the reaction mixture as confirmed with GC-MS. The precipitate was washed with Et_2O (5 $cm^3\times 3$) and dried in vacuo. Yellow powder of [*trans*-Pd(PMe_3)$_2$(SPh)$_2$] was obtained in 27% yield (23 mg).

^{1}H NMR (90 MHz, CD_2Cl_2) δ = 1.32 (t, 18H, *J* = 3.41 Hz, virtual coupling, P*Me*$_3$), 6.90—7.20, 7.48—7.62 (m, 10H, S*Ph*); ^{13}C{^{1}H} NMR (67.9 MHz, $CDCl_3$) δ = 13.7 (t, *J* = 13.3 Hz, virtual coupling, P*Me*$_3$), 127.0 (s), 127.8 (s), 131.3 (s), 147.4 (s, aromatic C); ^{31}P{^{1}H} NMR (109.4 MHz, $CDCl_3$): δ = −12.8 (s); IR 944 cm^{-1} (ν_{P-C}); Mp 141—146 °C (in air, decomp).

Reaction of 3a with MeI. MeI (0.0115 cm^3, 0.17 mmol) was added to an acetone solution (2 cm^3) of **3a** (61 mg, 0.17 mmol) at room temperature and the solution was stirred for 42 h at room temperature. The color of the solution was changed to yellow. Ethyl acetate was observed with GC-MS from the fraction collected by the trap-to-trap distillation of the reaction solution. The residue was washed with Et_2O (5 $cm^3\times 3$) and dried in vacuo. Yellow powder of [*trans*-Pd($COCH_3$)(I)(PMe_3)$_2$] was obtained in 34% yield (25 mg).

^{1}H NMR (90 MHz, CD_2Cl_2) δ = 1.46 (t, 18H, *J* = 3.63 Hz, virtual coupling, P*Me*$_3$), 2.35 (t, 3H, $^4J_{PH}$ = 1.43 Hz, C*H*$_3$COPd); ^{31}P{^{1}H} NMR (109.4 MHz, CD_2Cl_2) δ = −21.5 (s); ^{13}C{^{1}H} NMR (67.9 MHz) δ = 15.7 (t, *J* = 14.7 Hz, virtual coupling, P*Me*$_3$), 53.8 (t, $^2J_{PC}$ = 27.4 Hz, *C*H$_3$CO), 239.9 (s, CH$_3$*C*O); IR 1676 ($\nu_{C=O}$), 952 cm^{-1} (ν_{P-C}).

Preparation of [*trans*-PdC(=O)CH$_2$CH$_2$CH$_2$C(=O)O{P(CH$_3$)$_3$}$_2$]$_n$ 4a. An acetone solution (5 cm^3) of **1a** (277 mg, 0.875 mmol) and styrene (0.150 cm^3, 1.31 mmol) was stirred at room temperature for 20 h. Glutaric anhydride (100 mg, 0.876 mmol) was then added to the solution at room temperature and it was stirred for 25 h at room temperature. A white precipitate generated from the solution was filtered, washed with acetone (5 $cm^3\times 4$) and dried in vacuo to give a white powder of **4a** (63 mg, 17%).

^{1}H NMR (270 MHz, CD_2Cl_2) δ = 1.20 (t, 18H, *J* = 3.67 Hz, virtual coupling, P*Me*$_3$), 1.60—1.69 (m, 2H, CH$_2$*C*H$_2$CH$_2$), 1.97 (br. t, 2H, $^3J_{HH}$ = 6.97 Hz, C*H*$_2$COO), 2.53 (br. t, 2H, $^3J_{HH}$ = 7.67 Hz, C*H*$_2$CO); ^{13}C{^{1}H} NMR (67.9 MHz, CD_2Cl_2) δ = 14.2 (t, *J* = 13.3 Hz, virtual coupling, P*Me*$_3$), 21.9 (s, CH$_2$*C*H$_2$CH$_2$), 37.1 (s, *C*H$_2$COO), 56.0 (t, $^3J_{PC}$ = 16.1 Hz, *C*H$_2$CO), 177.8 (s, CH$_2$*C*OO), 239.3 (s, CH$_2$*C*O); ^{31}P{^{1}H} NMR (109.4 MHz, CD_2Cl_2) δ = −18.8 (s); IR 1665, 1645 ($\nu_{C=O}$, two absorption peaks were observed), 1599 (ν_{COO}), 948 cm^{-1} (ν_{P-C}). Found: C, 35.37; H 6.58%. Calcd for $C_{11}H_{24}O_3P_2Pd$: C, 35.37; H, 6.49%. Mp 94—96 °C (decomp).

Preparation of [*trans*-PdCOCH$_2$OCH$_2$COO{P(CH$_3$)$_3$}$_2$]$_n$ 4b. A THF (5 cm^3) solution of **1a** (336 mg, 1.06 mmol) and styrene (0.180 cm^3, 1.57 mmol) was stirred at room temperature for 17 h. Glycolic anhydride (126 mg, 1.09 mmol) dissolved in THF (5 cm^3) was added to the solution at room temperature and the solution was stirred for 6 h at room temperature. A white powder which precipitated from the solution was filtered, washed with THF (5 $cm^3\times 3$) and dried in vacuo to give a white powder of **4b** (216 mg, 54%).

^{1}H NMR (270 MHz, CD_2Cl_2, −30 °C) δ = 1.25 (t, 18H, *J* = 3.30 Hz, virtual coupling, P*Me*$_3$), 3.77 (br. s, 2H, C*H*$_2$), 3.95 (br. s, 2H, C*H*$_2$); ^{13}C{^{1}H} NMR (67.9 MHz, CD_2Cl_2, −30 °C) δ = 14.2 (t, *J* = 13.4 Hz, virtual coupling, P*Me*$_3$), 69.7 (s, *C*H$_2$COO), 82.0 (t, $^3J_{PC}$ = 13.7 Hz, *C*H$_2$COPd), 174.1 (s, CH$_2$*C*OO), 241.7 (s, CH$_2$*C*O); ^{31}P{^{1}H} NMR (109.4 MHz, CD_2Cl_2, −30 °C) δ = −17.9 (s); IR 1666, 1645 ($\nu_{C=O}$, two absorption peaks were observed), 1599 (ν_{COO}), 949 cm^{-1} (ν_{P-C}). Found: C, 31.73; H 5.60%. Calcd for $C_{10}H_{22}O_3P_2Pd$: C, 32.06; H, 5.92%. Mp 110—112 °C (decomp).

Preparation of [*trans*-PdCOCH$_2$CH$_2$COO{P(CH$_3$)$_3$}$_2$]$_n$ 4c. An Et_2O solution (5 cm^3) of **1a** (262 mg, 0.827 mmol) and styrene (0.115 cm^3, 1.00 mmol) was stirred at room temperature for 24 h. After the mixture was heated at 45 °C for 5 min, succinic anhydride (82 mg, 0.82 mmol) dissolved in acetone (5 cm^3) was added to the solution at room temperature and stirring was continued for 18 h at room temperature. A white precipitate which generated from the mixture was filtered, washed with Et_2O (5 $cm^3\times 3$) and dried in vacuo. Pale yellow powder of **4c** (52 mg, 18%) was obtained.

^{1}H NMR (270 MHz, $CDCl_3$, −20 °C) δ = 1.27 (t, 18H, *J* = 3.66 Hz, virtual triplet, P*Me*$_3$), 2.15—2.29 (m, 2H, C*H*$_2$CO), 2.82—2.98 (m, 2H, C*H*$_2$COO); ^{13}C{^{1}H} NMR (67.9 MHz, CD_2Cl_2, −20 °C) δ = 13.3 (t, *J* = 13.6 Hz, virtual coupling, P*Me*$_3$), 31.5 (s, *C*H$_2$COO), 52.3 (br. s, *C*H$_2$COPd), 176.8 (s, CH$_2$*C*OO), 238.5 (br. s, CH$_2$*C*O); ^{31}P{^{1}H} NMR (109.4 MHz, $CDCl_3$, −20 °C) δ = −19.2 (s); IR 1665 ($\nu_{C=O}$), 1589 (ν_{COO}), 948 cm^{-1} (ν_{P-C}). Found:

C, 33.58; H, 6.52%. Calcd for $C_{10}H_{22}O_3P_2Pd$: C, 33.49; H, 6.18%. Mp 89—91 °C (decomp).

Preparation of [Pd(C$_6$H$_4$COO){P(CH$_3$)$_3$}$_2$] 4d. A THF (5 cm^3) solution of **1a** (327 mg, 1.03 mmol) and styrene (0.355 cm^3, 3.10 mmol) was stirred at 50 °C for 3 h. Then phthalic anhydride (162 mg, 1.09 mmol) was added to the solution at room temperature and stirring was continued for 24 h at room temperature. The color of the solution changed from yellow to deep red and a white precipitate was generated from the mixture. The precipitate was filtered, washed with THF (5 cm^3×6) and dried in vacuo to give a powder of **4d** (89 mg, 23%).

^{1}H NMR (270 MHz, CD_2Cl_2, −30 °C) δ = 1.45 (d, 9H, $^2J_{PH}$ = 8.79 Hz, P*Me*$_3$), 1.66 (d, 9H, $^2J_{PH}$ = 10.3 Hz, P*Me*$_3$), 7.02—7.60 (m, 4H, aromatic H); ^{13}C{^{1}H} NMR (67.9 MHz, CD_2Cl_2, −30 °C) δ = 15.0 (d, $^1J_{PC}$ = 22.5 Hz, P*Me*$_3$), 18.1 (dd, $^1J_{PC}$ = 31.2 Hz, $^3J_{PC}$ = 2.89 Hz, P*Me*$_3$), 124.6 (s), 130.16 (d, J_{PC} = 3.90 Hz), 130.36 (dd, J_{PC} = 9.08, 2.89 Hz), 133.15 (dd, J_{PC} = 3.90, 9.65 Hz), 143.8 (s), 157.2 (d, $^2J_{PC}$ = 124.1 Hz, aromatic C), 181.1 (d, $^3J_{PC}$ = 9.65 Hz, *C*OO); ^{31}P{^{1}H} NMR (109 MHz, CD_2Cl_2, −30 °C): δ = −17.3 (d, $^2J_{PP}$ = 41.5 Hz), −3.37 (d, $^2J_{PP}$ = 41.5 Hz); IR 1611 (ν_{COO}), 948 cm^{-1} (ν_{PC}). Found: C, 41.11; H 5.67%. Calcd for $C_{13}H_{22}O_2P_2Pd$: C, 41.23; H, 5.86%. Mp 93—95 °C (decomp).

Reaction of 4d with CO. A CD_2Cl_2 solution (0.5 cm^3) of **4d** (7.4 mg, 0.018 mmol) was treated with CO (1 atm) and the progress of the reaction at room temperature was monitored by NMR. After 24 h, phthalic anhydride was formed in the reaction mixture in 77% yield as determined with ^{1}H NMR.

Phthalic anhydride: ^{1}H NMR (270 MHz) δ = 7.85—8.15 (m); ^{13}C{^{1}H} NMR (67.9 MHz) δ = 125.3 (s), 130.9 (s), 135.8 (s), 162.6 (s). These chemical shifts are identical with those of the authentic sample.

Reaction of 4d with PhCOOH. Benzoic acid (2.2 mg, 0.018 mmol) was added to a CD_2Cl_2 (0.5 cm^3) solution containing **4d** (7.2 mg, 0.018 mmol) and ^{1}H NMR change was followed by allowing the solution to stand for 93 h at room temperature. [*cis*-Pd(PMe$_3$)$_2$(OCOPh)$_2$] was generated in 83% yield as determined by ^{1}H NMR.

[*cis*-Pd(PMe$_3$)$_2$(OCOPh)$_2$]: ^{1}H NMR (270 MHz) δ = 1.56—1.64 (filled-in-doublet, 18H, P*Me*$_3$), 7.25—7.50 (m, 6H), 7.90—8.00 (m, 4H, aromatic H); ^{13}C{^{1}H} NMR (67.9 MHz) δ = 14.5—1.6 (five-line multiplet,[24] P*Me*$_3$), 127.3 (s), 129.2 (s), 130.1 (s), 135.6 (s, aromatic C), 171.2 (s, Ph*C*OO); ^{31}P{^{1}H} NMR (109.4 MHz) δ = −1.26 (s).

Catalytic Hydrogenation of Anhydrides by a Palladium Complex. A typical procedure is as follows; a THF solution (5 cm^3) of the anhydride (2 mmol) and [Pd(PPh$_3$)$_4$] (0.02 mmol) was placed in a 100 cm^3 stainless autoclave purged with argon. The autoclave was pressurized with dihydrogen (3.0 MPa at room temperature) and the solution was stirred for 24 h at 80 °C. After the autoclave was cooled with liquid nitrogen until the internal pressure became 2.0 MPa, the dihydrogen pressure was released. The products were identified with GC, GC-MS, and ^{1}H NMR and by comparison with corresponding authentic samples.

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