Oxidative Addition of Aryl and Benzyl Trifluoroacetates to Zerovalent Palladium Complexes with Two Modes of C–O Bond Cleavage Processes

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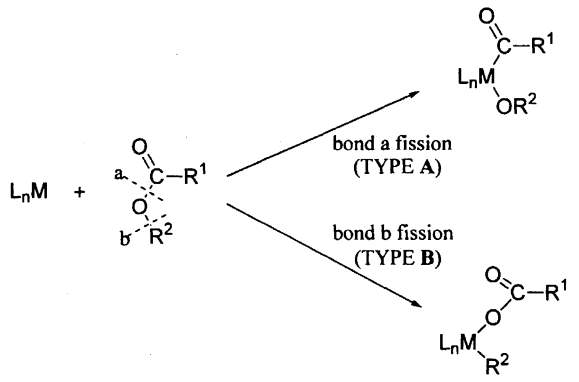
The aryl trifluoroacetates oxidatively added to a zerovalent palladium complex **2a** with acyl-O bond cleavage under mild conditions to give the corresponding *trans*-(aryloxo)(trifluoroacetyl)palladium complexes **3a—3c**. But 4-nitrophenyl trifluoroacetate reacted with **2a** to yield *cis*-[Pd(OC_6H_4-4-NO_2)$_2$(PMe_3)$_2$] **3d**, which was produced with C–O bond activation followed by disproportionation reaction. In contrast, benzyl trifluoroacetates reacted with the Pd(0) complex with benzyl–O bond fission to form benzyl(trifluoroacetato)palladium complexes **4a—4d**. Complexes **4a—4d** are in equilibrium in solutions between *trans* and *cis* isomers, with the proportion of the *cis* isomer increasing in polar solvents. Palladium-catalyzed carbonylation of benzyl trifluoroacetate has been achieved in the presence of benzyl alcohol and triethylamine to yield benzyl phenylacetate.

In contrast to the well-utilized transition metal-catalyzed processes involving the carbon–halogen bond cleavage,[1] catalytic processes using carbon–oxygen bond cleavage have been less explored, except for the palladium-catalyzed processes using allylic esters.[2] There are two possible modes in the cleavage of carboxylic esters on interaction with a low valent transition metal complex: Type A involves the cleavage of the acyl–O bond in an ester to give an acyl–alkoxide type complex and Type B is concerned with the carboxylato–carbon bond cleavage to give an organo-carboxylato type complex (Scheme 1).[3]

The point of cleavage may depend on the carboxylic ester and on the properties of the transition metal complex employed. The Type B process seems to take place more easily with allylic and benzylic esters. We have previously reported that nickel(0) complexes react with carboxylic esters under mild conditions to cause two types of C–O bond cleavage reactions. Aryl carboxylates[4] were found to undergo the acyl–aryloxide cleavage on interaction with Ni(0) complexes via type **A** fission, whereas allylic compounds reacted with Ni(0)[4b] and Pd(0)[5] complexes to give η^3-allylmetal(II) complexes through the type **B** process.



Scheme 1. Two modes of C–O bond cleavage of esters by transition metal complexes.

Recently we have been concerned with the study of oxidative addition of carbonyl-containing organic compounds to palladium complexes in order to explore the possibility of finding new palladium-catalyzed synthetic processes. Nickel and palladium complexes somewhat differ in their reactivities to cause oxidative addition and subsequent reactions. Palladium complexes were expected to provide a better chance of realizing catalytic processes, as can be seen from the wide variety of applications utilizing palladium catalysts. In fact, on the basis of our studies on the oxidative addition reaction of carboxylic anhydrides to zerovalent palladium complexes affording acyl(carboxylato) type palladium complexes and their reactivities towards various substrates, particularly dihydrogen,[6] we have developed a new catalytic process of converting carboxylic anhydrides to aldehydes and carboxylic acids. Further exploration of the information on the properties of the organopalladium complexes led us to the discovery of a novel palladium-catalyzed direct hydrogenation of carboxylic acids into aldehydes.[7]

The Pd(0) complexes are usually less electron-rich than the corresponding Ni(0) complexes. Thus unactivated carboxylic esters without electron-withdrawing substituents such as methyl formate, methyl acetate, methyl propionate and phenyl propionate proved unreactive with Pd(0) complexes even on heating at 40 °C. In contrast [Ni(cod)$_2$] (cod = 1,5-cyclooctadiene) in the presence of tertiary phosphines and bipyridine ligands readily react with ethyl formate[4a] and phenyl acetate or propionate to undergo the acyl–O cleavage reactions.[4] For enhancing the reactivity of the reactants to undergo the C–O bond cleavage on interaction with Pd(0) complexes, we examined the reactions of carboxylic esters

having electron-withdrawing groups with coordinatively unsaturated zero-valent palladium complexes. In fact aryl and benzyl trifluoroacetates were found to undergo the oxidative addition readily on interaction with Pd(0) complexes.

Here we report the C–O bond cleavage of these activated esters on interaction with zerovalent palladium complexes,[8,9] together with some attempts to apply the information gained to catalytic carbonylation processes.

Results and Discussion

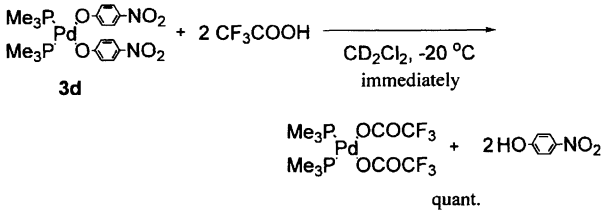
The styrene-coordinated Pd(0) complex, [Pd(styrene)-$(PMe_3)_2$] **2a**,[10] prepared in situ by thermolysis of $[PdEt_2(PMe_3)_2]$ **1a**,[11] in the presence of styrene, was found to react readily at room temperature with aryl trifluoroacetates having various para-substituents Y (Y = H, Me, and CN) resulting in the acyl–O bond cleavage to give *trans*-(aryloxo)-(trifluoroacetyl)bis(trimethylphosphine)palladium(II) complexes **3a**—**3c**, as shown in Scheme 2.

The (aryloxo)(trifluoroacetyl)palladium(II) complexes[12] have been characterized with spectroscopic means and by elemental analysis. The *trans* configuration of the products **3a**—**3c** was determined on the basis of the ^1H and $^{13}C\{^1H\}$ NMR spectra. In particular, signals of the methyl groups in the coordinated PMe_3 ligands were observed as virtual triplets, in support of the *trans* configuration. The $^{31}P\{^1H\}$ NMR spectra of these compounds showed a singlet. Complexes **3a**—**3c** are thermally unstable and undergo slow decomposition in solution even at −20 °C.

On the other hand, reaction of **2a** with 4-nitrophenyl trifluoroacetate at room temperature gave *cis*-$[Pd(OC_6H_4\text{-}4\text{-}NO_2)_2(PMe_3)_2]$ **3d**[13] as the sole isolable product precipitated from the reaction mixture (Scheme 3).

The bis(nitrophenoxo)palladium complex is considered to be formed by oxidative addition of the ester with acyl–O bond cleavage, yielding an acyl(aryloxo)palladium intermediate; this further undergoes the disproportionation reaction, yielding **3d** and unidentified compounds. Our attempts to follow the reaction course to establish the route to produce the *cis*-bis(aryloxo)palladium complex in the reaction mixture were frustrated by occurrence of decomposition, causing the precipitation of a black precipitate from the supernatant of the reaction mixture. The *cis* configuration of the complex **3d** is based on observation of no virtual triplet ascribable to the *trans*-situated PMe_3 ligands in the ^1H and ^{13}C NMR. Instead, the ^1H NMR signal of the PMe_3 ligands was observed as a filled-in-doublet, and the $^{13}C\{^1H\}$ NMR spectrum of the PMe_3 signals in **3d** showed a six-line-multiplet. These NMR results are in agreement with the previously observed NMR spectra of *cis* complexes coordinated with PPh_2Me or PMe_2Ph ligands.[14] The IR spectrum of **3d** exhibiting a doublet ν_{P-C} stretching band at 969 and 946 cm^{-1} also supports the *cis* configuration.

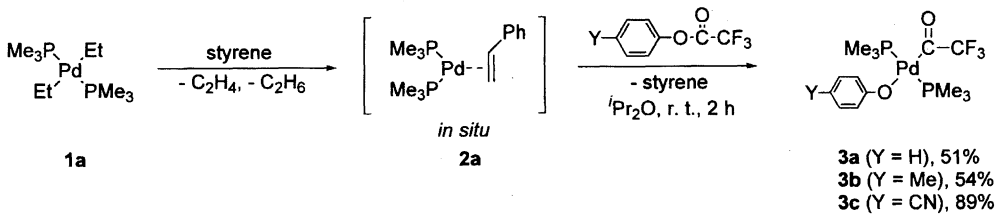
Complex **3d** was quantitatively converted into two mol amt. of 4-nitrophenol and *cis*-$[Pd(OOCCF_3)_2(PMe_3)_2]$ on its treatment with 2 mol amt. of CF_3COOH at −20 °C, as confirmed by NMR spectroscopy.



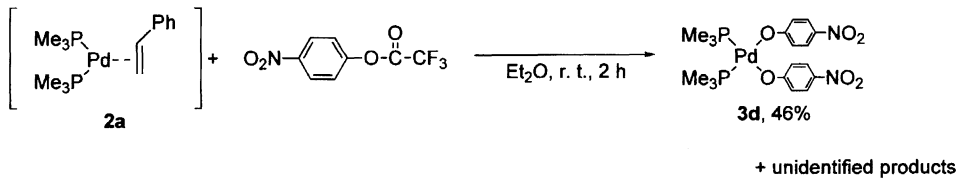
(1)

In contrast to the reactions of **2a** with aryl trifluoroacetates, the reaction of Pd(0) complexes having PMe_3 and PPh_2Me ligands with benzyl trifluoroacetates at room temperature caused the cleavage of the C–O bond between the benzyl and trifluoroacetato entities, affording benzyl(trifluoroacetato)-palladium(II) complexes: $[Pd(CH_2C_6H_4\text{-}4\text{-}Y)(OOCCF_3)$-$(PMeR_2)_2]$ (Y = H, NO_2, R = Me, Ph) **4a**—**4d** (Scheme 4).

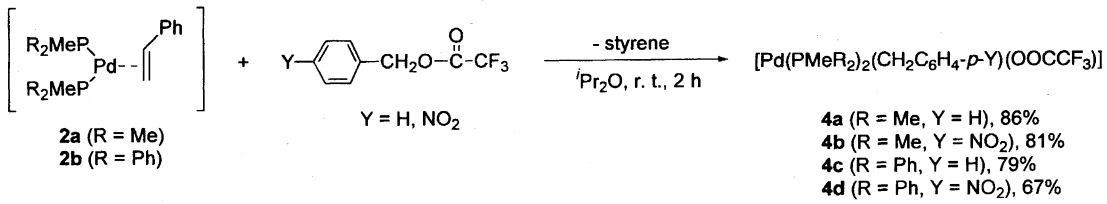
The complexes **4a**—**4d** are observed as a mixture of the *trans* and the *cis* isomers in solution as revealed by the ^1H and $^{31}P\{^1H\}$ NMR. The *trans* : *cis* isomer ratio in solutions varied depending on the solvent used and the para substituent in the benzyl ligand, as shown in Table 1. It can be seen that the *trans* isomers dominate in less polar solvents, but the ratio of the *cis* isomer increases in polar solvents. The trend is



Scheme 2. Oxidative addition of aryl trifluoroacetates to **2a** with acyl–O bond cleavage.

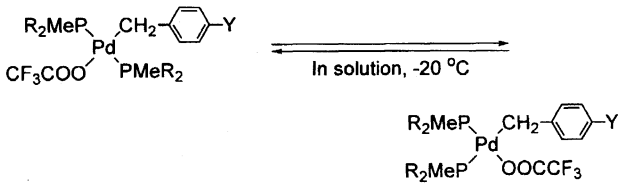


Scheme 3. Reaction of **2a** with 4-nitrophenyl trifluoroacetate.



Scheme 4. Oxidative addition of benzyl trifluoroacetates with benzyl–O bond cleavage.

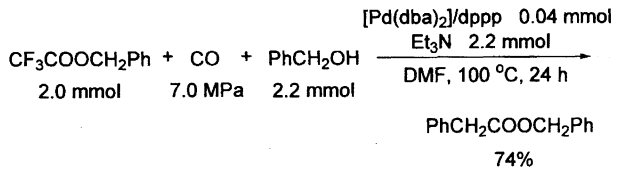
Table 1. *trans–cis* Equilibrium of **4a—4d**



Complex	Solvent	*trans* : *cis*
4a	Acetone-d_6	96 : 4
4b	Toluene-d_8	97 : 3
	CD_2Cl_2	86 : 14
	Acetone-d_6	73 : 27
	CD_3NO_2	60 : 40
4c	Acetone-d_6	72 : 28
4a	Acetone-d_6	53 : 47
	Toluene-d_8	82 : 18

in agreement with the previous observation of the *trans* and *cis* equilibration of palladium dichlorides having $PMePh_2$ and PMe_2Ph ligands that the *cis* isomers are favored in polar solvents because of the stronger interaction of the polar solvent molecules with the *cis* isomers having the higher dipole moments.[15] Variation of the temperature caused little change in the *trans* : *cis* ratios.

We attempted to develop a catalytic carbonylation of benzyl trifluoroacetate by a palladium complex using the information of the palladium-promoted benzyl–O bond cleavage in the benzyl trifluoroacetate. It was found that the benzyl trifluoroacetate was converted under CO pressure into benzyl phenylacetate when the reaction was carried out in the presence of $[Pd(dba)_2]$ and 1,3-bis(diphenylphosphino)propane (dppp) ligand and triethylamine as the base, as shown in Eq. 2.[16]



(2)

Employment of other nucleophiles, such as methanol and diethyl amine instead of benzylalcohol in combination with triethylamine was unsuccessful because of their high reactivity towards benzyl trifluoroacetate. The catalytic carbonylation reaction is considered to proceed through oxidative addition of benzyl trifluoroacetate to give benzyl(trifluoroacetato)palladium intermediate. The ensuing CO insertion into the benzyl–palladium bond to give a phenylacetyl–palladium intermediate, followed by its reaction with benzyl alcohol and triethylamine accounts for the formation of the benzyl phenylacetate. In previous studies of the benzyl- and phenylacetylpalladium complexes with nucleophiles under carbon monoxide,[17] it was established that the CO insertion into the benzyl–palladium bond gave the phenylacetylpalladium complex and its subsequent reactions with alcohols and tertiary amine released the phenylacetates.

Conclusion

We demonstrated here the two modes of C–O bond cleavage of esters by zerovalent palladium complexes. When a palladium complex reacts with the aryl trifluoroacetates, palladium will attack the highly activated carbonyl carbon and acyl–O bond fission will take place because the aryloxide is a relatively good leaving group. On the other hand, in the reaction of Pd(0) with benzyl trifluoroacetates, Pd(0) will preferentially attack the benzyl carbon with the elimination of the trifluoroacetate as a leaving group.

Experimental

All manipulations were carried out under argon using Schlenk tube technique. Solvents were purified by the usual methods under argon. Palladium dichloride was purchased from Tanaka-Kikinzoku Co. and used without purification. Phenyl trifluoroacetate (Tokyo Kasei Kogyo Co.) and 4-nitrophenyl trifluoroacetate (Aldrich) were commercial products, and other trifluoroacetic acid esters were synthesized by the reaction of trifluoroacetic anhydride with corresponding alcohols or phenols in the presence of triethylamine. NMR data were obtained on a JEOL EX-270 or a JEOL GSX-400 instrument. Trifluoroacetic acid in $CDCl_3$ was used as an external standard in ^{19}F NMR measurement. The chemical shifts in $^{31}P\{^1H\}$ NMR are in ppm from external 85%-H_3PO_4. The multiplicities 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 separations between the peaks and do not reflect the true coupling constants. IR spectra were obtained on Perkin Elmer Paragon 1000. Melting points were measured under argon. Gas chromatography was carried out on a Hitachi 263-50 equipped with OV-1701. Low-resolution mass spectra combined with gas chromatograph results were obtained with a JEOL JMS-SX102A.

Preparation of *trans*-[Pd(COCF$_3$)(OC$_6$H$_4$-*p*-Y){P(CH$_3$)$_3$}$_2$] 3a—3c. These (aryloxo)(trifluoroacetyl)palladium complexes were prepared in a similar manner. As an 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 (Y = H); A $^iPr_2O$ (5 cm^3) solution of $[PdEt_2(PMe_3)_2]$ (558 mg, 1.76 mmol) and styrene (0.606 cm^3, 5.29 mmol) was heated at 50 °C for 1 h. After the solution was cooled at room temperature, $CF_3COOC_6H_5$ (335 mg, 1.76 mmol) was added to the solution and

the solution was stirred at room temperature for 2 h. The white precipitate which was generated from the solution was filtered, washed with Et_2O (5 $cm^3 \times 2$) and dried in vacuo. White powder of **3a** was obtained in 51% (413 mg, 0.993 mmol) yield.

^{1}H NMR (270 MHz, CD_2Cl_2, −20 °C) δ = 1.22 (t, 18H, J = 3.85 Hz, virtual coupling, P*Me*$_3$), 6.32—6.39 (m, 1H), 6.72—6.78 (m, 2H), 6.93—7.03 (m, 2H, aromatic H); ^{13}C{^{1}H} NMR (67.9 MHz, CD_2Cl_2, −20 °C) δ = 12.2 (t, J = 14.9 Hz, virtual coupling, P*Me*$_3$), 112.1 (s), 113.4 (tq, $^1J_{FC}$ = 300.0 Hz, $^3J_{PC}$ = 11.5 Hz, CO*C*F$_3$), 118.9 (s), 128.4 (s), 168.5 (s, aromatic C), 227.8—229.8 (m, *C*OCF$_3$); ^{19}F NMR (254 MHz, CD_2Cl_2, −20 °C) δ = −77.4 (s); ^{31}P{^{1}H} NMR (109 MHz, CD_2Cl_2, −20 °C) δ = −16.4 (s); IR 1680 ($\nu_{C=O}$), 954 cm^{-1} (ν_{P-C}). Found: C, 37.56; H, 5.10%. Calcd for $C_{14}H_{23}O_2F_3P_2Pd$: C, 37.48; H, 5.17%. Mp 76.0−77.0 °C (decomp).

3b (Y = Me): White powder (54%); ^{1}H NMR (270 MHz, acetone-d_6, −20 °C) δ = 1.27 (t, 18H, J = 14.9 Hz, virtual coupling, P*Me*$_3$), 2.09 (s, 3H, C$_6$H$_4$C*H*$_3$), 6.58—6.68 (m, 2H), 6.72—6.82 (m, 2H, aromatic H); ^{13}C{^{1}H} NMR (67.9 MHz, CD_2Cl_2, −20 °C) δ = 13.2 (t, J = 14.8 Hz, virtual coupling, P*Me*$_3$), 20.2 (s, C$_6$H$_4$*C*H$_3$), 114.1 (tq, $^1J_{FC}$ = 300.1 Hz, $^3J_{PC}$ = 11.3 Hz, CO*C*F$_3$), 119.0 (s), 121.3 (s), 129.6 (s), 166.8 (s, aromatic C), 229.2—231.1 (m, *C*OCF$_3$); ^{19}F NMR (254 MHz, acetone-d_6, −20 °C) δ = −77.6 (s); ^{31}P{^{1}H} NMR (109 MHz, acetone-d_6, −20 °C) δ = −14.5 (s); IR 1667 ($\nu_{C=O}$), 954 cm^{-1} (ν_{P-C}). Found: C, 39.15; H, 5.72%. Calcd for $C_{15}H_{25}O_2F_3P_2Pd$: C, 38.96; H, 5.45%. Mp 80.0—81.0 °C (decomp).

3c (Y = CN): White powder (89%); ^{1}H NMR (270 MHz, CD_2Cl_2, −20 °C) δ = 1.22 (t, 18H, J = 3.85 Hz, virtual coupling, P*Me*$_3$), 6.72—6.84 (m, 2H), 7.28—7.36 (m, 2H, aromatic H); ^{13}C{^{1}H} NMR (67.9 MHz, CD_2Cl_2, −20 °C) δ = 13.2 (t, J = 14.3 Hz, virtual coupling, P*Me*$_3$), 93.9 (s, aromatic C), 113.7 (tq, $^1J_{FC}$ = 298.8 Hz, $^3J_{PC}$ = 11.9 Hz, CO*C*F$_3$), 120.2 (s, aromatic C), 121.7 (s, *C*N), 133.9 (s), 173.5 (s, aromatic C), 226.9 (tq, $^2J_{FC}$ = 36.6 Hz, $^2J_{PC}$ = 4.8 Hz, *C*OCF$_3$); ^{19}F NMR (254 MHz, CD_2Cl_2, −20 °C) δ = −77.8 (s); ^{31}P{^{1}H} NMR (109 MHz, CD_2Cl_2, −20 °C) δ = −15.8 (s); IR 2213 (ν_{CN}), 1681 ($\nu_{C=O}$), 951 cm^{-1} (ν_{P-C}). Found: C, 38.16; H, 4.92; N, 3.31%. Calcd for $C_{15}H_{22}O_2NF_3P_2Pd$: C, 38.03; H, 4.68; N, 2.96%. Mp 84.0—86.0 °C (decomp).

Preparation of *cis*-[Pd(OC$_6$H$_4$-*p*-NO$_2$)$_2${P(CH$_3$)$_3$}$_2$] 3d. An Et_2O (5 cm^3) solution of [PdEt$_2$(PMe$_3$)$_2$] (402 mg, 1.27 mmol) and styrene (0.440 cm^3, 3.84 mmol) was heated at 30 °C for 51 h. After the solution was cooled at room temperature, $CF_3COOC_6H_4$-*p*-NO_2 (305 mg, 1.30 mmol) was added to the solution and the reaction mixture was stirred at room temperature for 2 h. The yellow precipitate generated from the solution was filtered, washed with Et_2O (10 $cm^3 \times 4$) and dried in vacuo. The yellow powder of **3d** was obtained in 46% (311 mg, 0.581 mmol) yield. ^{1}H NMR (270 MHz, CD_2Cl_2, r.t.) δ = 1.52—1.57 (filled-in-doublet, 18H, P*Me*$_3$), 6.65—6.80 (m, 4H), 7.85—7.95 (m, 4H, aromatic H); ^{13}C{^{1}H} NMR (67.9 MHz, CD_2Cl_2, −20 °C) δ = 14.6 (six-line-multiplet,[14] $|^1J_{PC}+^3J_{PC}|$ = 36.3 Hz, P*Me*$_3$), 118.6 (s), 125.8 (s), 135.5 (s), 175.0 (s, aromatic C); ^{31}P{^{1}H} NMR (109 MHz, CD_2Cl_2, r.t.) δ = 0.74 (s); IR 969, 946 cm^{-1} (ν_{P-C}). Found: C, 40.20; H, 5.06; N, 5.04%. Calcd for $C_{24}H_{26}O_6N_2P_2Pd$: C, 40.43; H, 4.90; N, 5.24%. Mp 85.5—86.5 °C (decomp).

Reaction of 3d with Trifluoroacetic Acid. A CD_2Cl_2 solution (0.5 cm^3) of **3d** (12.3 mg, 0.023 mmol) was treated with 2 mol amt. of CF_3COOH (0.0036 cm^3, 0.047 mmol) at −20 °C in an NMR tube. The color of the solution immediately changed from yellow to colorless. Quantitative formation of 4-nitrophenol and *cis*-[Pd(OOCCF$_3$)$_2${P(CH$_3$)$_3$}$_2$] was observed as determined by NMR.

^{1}H NMR (270 MHz, −20 °C) δ = 1.55—1.62 (filled-in-doublet, 18H, *Me*$_3$P of *cis*-[Pd(OOCCF$_3$)$_2${P(CH$_3$)$_3$}$_2$]), 6.40—7.00 (br., overlapping, 2H), 6.95—7.05 (m, 4H), and 8.07—8.15 (m, 4H, 2 mol amt. of 4-nitrophenol); ^{13}C{^{1}H} NMR (67.9 MHz, r.t.) δ = 14.8—16.0 (five-line-multiplet,[14] $|^1J_{PC}+^3J_{PC}|$ = 38.0 Hz, *Me*$_3$P of *cis*-[Pd(OOCCF$_3$)$_2${P(CH$_3$)$_3$}$_2$]), 116.5 (q, $^1J_{FC}$ = 290.9 Hz, *C*F$_3$COO of *cis*-[Pd(OOCCF$_3$)$_2${P(CH$_3$)$_3$}$_2$]), 116.1 (s), 126.4 (s), 141.5 (s), and 163.0 (s, aromatic C of 4-nitrophenol), 162.5 (q, $^2J_{FC}$ = 37.1 Hz, CF_3COO of *cis*-[Pd(OOCCF$_3$)$_2${P(CH$_3$)$_3$}$_2$]); ^{19}F NMR (254 MHz, −20 °C) δ = −75.2 (s); ^{31}P{^{1}H} NMR (109 MHz, −20 °C) δ = 3.78 (s).

Preparation of [Pd(CH$_2$C$_6$H$_4$-*p*-Y)(OCOCF$_3$)(PCH$_3$R$_2$)$_2$] 4a—4d. Complexes **4a**—**4d** were synthesized in a similar way. As an example, preparation of **4a** is described below.

4a (R = H, Y = H): A ^{i}Pr$_2$O (5 cm^3) solution of [PdEt$_2$(PMe$_3$)$_2$] (320 mg, 1.01 mmol) and styrene (0.345 cm^3, 3.01 mmol) was heated at 50 °C for 3 h. After the solution was cooled at room temperature, $CF_3COOCH_2C_6H_5$ (210 mg, 1.03 mmol) was added to the solution and the solution was stirred at room temperature for 2 h. The white precipitate which was generated from the solution was filtered, washed with pentane (5 $cm^3 \times 3$) and dried in vacuo. A white powder of **4a** was obtained in 86% (401 mg, 0.867 mmol) yield. ^{1}H NMR (270 MHz, acetone-d_6, −20 °C) δ = 1.21 (t, 17.18H, J = 3.30 Hz, virtual coupling, P*Me*$_3$ of *trans*-**4a**), 1.29 (d, 0.41H, $^3J_{PH}$ = 8.43 Hz, P*Me*$_3$ of *cis*-**4a**), 1.65 (d, 0.41H, $^3J_{PH}$ = 11.0 Hz, P*Me*$_3$ of *cis*-**4a**), 2.59 (t, 1.91H, $^3J_{PH}$ = 8.06 Hz, C*H*$_2$Ph of *trans*-**4a**), 2.93 (br. d, 0.09H, $^3J_{PH}$ = 9.16 Hz, C*H*$_2$Ph of *cis*-**4a**), 7.00—7.50 (m, 5H, CH$_2$*Ph* of *trans*- and *cis*-**4a**); ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, r.t., only signals of *trans*-**4a** were observed) δ = 13.0 (t, J = 13.6 Hz, virtual coupling, P*Me*$_3$), 14.4 (t, J = 2.94 Hz, *C*H$_2$Ph), 117.1 (q, $^1J_{FC}$ = 292.7 Hz, OCO*C*F$_3$), 124.8 (br. s), 128.3 (s), 129.8 (t, $^3J_{PC}$ = 2.20 Hz), 147.1 (s, aromatic C), 161.2 (q, $^2J_{FC}$ = 34.5 Hz, O*C*OCF$_3$); ^{19}F NMR (254 MHz, acetone-d_6, −20 °C) δ = −73.9 (s); ^{31}P{^{1}H} NMR (109 MHz, acetone-d_6, −20 °C) δ = −13.6 (s, 1.86P, *P*Me$_3$ of *trans*-**4a**), −22.0 (AB quartet, 0.07P, $^2J_{PP}$ = 47.7 Hz, *P*Me$_3$ of *cis*-**4a**), −4.45 (AB q, 0.07P, $^2J_{PP}$ = 47.7 Hz, *P*Me$_3$ of *cis*-**4a**); IR 1694 ($\nu_{C=O}$), 1414 (ν_{COO}), 949 cm^{-1} (ν_{P-C}). Found: C, 38.97; H, 5.36%. Calcd for $C_{15}H_{25}O_2F_3P_2Pd$: C, 38.96; H, 5.45%. Mp 96.2—97.0 °C (decomp).

4b (R = H, Y = NO_2): Yellow powder (81%). ^{1}H NMR (270 MHz, acetone-d_6, −20 °C) δ = 1.28 (t, J = 3.48 Hz, 13.38H, virtual coupling, P*Me*$_3$ of *trans*-**4b**), 1.33 (d, $^2J_{PH}$ = 8.79 Hz, 2.31H, P*Me*$_3$ of *cis*-**4b**), 1.68 (d, $^2J_{PH}$ = 11.4 Hz, 2.31H, P*Me*$_3$ of *cis*-**4b**), 2.73 (t, $^3J_{PH}$ = 8.06 Hz, 1.47H, C*H*$_2$Ph of *trans*-**4b**), 2.80 (dd, $^3J_{PH}$ = 11.7, 3.67 Hz, 0.53H, C*H*$_2$Ph of *cis*-**4b**), 7.30—7.45 and 7.90—8.00 (m, 1.08H, aromatic H of *cis*-**4b**), 7.60—7.70 (m) and 8.05—8.15 (m, 2.92H, aromatic H of *trans*-**4b**), 7.30—7.45 and 7.90—8.00 (m, 1.08H, aromatic H of *cis*-**4b**); ^{13}C{^{1}H} NMR (67.9 MHz, $CDCl_3$, −20 °C, only signals of *trans*-**4b** were observed) δ = 12.5 (t, J = 14.3 Hz, virtual coupling, P*Me*$_3$), 13.4 (t, $^2J_{PC}$ = 3.6 Hz, *C*H$_2$Ph), 116.5 (q, *C*F$_3$COO, $^1J_{FC}$ = 292.1 Hz), 123.4 (s), 129.9 (t, $^4J_{PC}$ = 1.59 Hz), 144.6 (s), 158.6 (s, CH$_2$*C*$_6$H$_4$-4-NO$_2$), 160.6 (q, $^2J_{FC}$ = 35.0 Hz, CF$_3$*C*OO); ^{19}F NMR (254 MHz, acetone-d_6, −20 °C) showed one singlet: δ = −74.0 (s); ^{31}P{^{1}H} NMR (109 MHz, acetone-d_6, −20 °C) δ = −13.4 (s, 1.48P, *P*Me$_3$ of *trans*-**4b**), −16.6 (AB quartet, 0.26P, $^2J_{PP}$ = 46.3 Hz, *P*Me$_3$ of *cis*-**4b**), −3.07 (AB q, 0.26P, $^2J_{PP}$ = 46.3 Hz, *P*Me$_3$ of *cis*-**4b**); IR 1680 ($\nu_{C=O}$), 1414 (ν_{COO}), 947 cm^{-1} (ν_{P-C}). Found: C, 35.68; H, 4.72; N, 2.72%. Calcd for $C_{15}H_{24}O_4NF_3P_2Pd$: C, 35.48; H, 4.76, N, 2.76%. Mp 93.5—94.5 °C (decomp).

4c (R = Ph, Y = H): White powder (79%). ^{1}H NMR (270 MHz, acetone-d_6, −20 °C) δ = 1.49 (d, 0.80H, $^3J_{PH}$ = 7.69 Hz, P*Me*$_3$ of

cis-**4c**), 1.85 (t, 4.40H, J = 3.12 Hz, virtual coupling, P*Me*$_3$ of *trans*-**4c**), 1.92 (d, 0.80H, $^3J_{PH}$ = 9.89 Hz, P*Me*$_3$ of *cis*-**4c**), 2.41 (t, 1.43H, $^3J_{PH}$ = 7.33 Hz, C*H*$_2$Ph of *trans*-**4c**), 3.00 (d, 0.57H, $^3J_{PH}$ = 9.52 Hz, C*H*$_2$Ph of *cis*-**4c**), 6.32—7.80 (m, 25H, aromatic H); ^{13}C{^{1}H} NMR (67.9 MHz, toluene-d_8, −20 °C, only signals of *trans*-**4c** were obtained) δ = 11.2 (t, J = 13.5 Hz, virtual coupling, P*Me*$_3$), 19.6 (br. s, *C*H$_2$Ph), 117.4 (q, $^1J_{FC}$ = 292.9 Hz, *C*F$_3$COO), 124.4 (s), 124.7 (s, overlapped with the signal of toluene-d_8), 129.7 (s, overlapped with toluene-d_8), 146.0 (s, CH$_2$*Ph*), 128.6 (t, J_{PC} = 5.04 Hz), 130.2 (s), 132.3 (t, J_{PC} = 21.5 Hz), 133.1 (t, J_{PC} = 6.39 Hz, virtual coupling, PMe*Ph*$_2$), 161.0 (q, $^2J_{FC}$ = 35.0 Hz, CF$_3$*C*OO); ^{19}F NMR (254 MHz, acetone-d_6, −20 °C) δ = −75.2 (s); ^{31}P{^{1}H} NMR (109 MHz, acetone-d_6, −20 °C) δ = 12.7 (s, 1.40P, *P*Me$_3$ of *trans*-**4c**), 6.40 (AB q, 0.30P, $^2J_{PP}$ = 47.0 Hz, *P*Me$_3$ of *cis*-**4c**), 18.5 (AB q, 0.30P, $^2J_{PP}$ = 47.0 Hz, *P*Me$_3$ of *cis*-**4c**); IR 1680 ($\nu_{C=O}$), 1436 (ν_{COO}), 892 cm^{-1} (ν_{P-C}). Found: C, 59.04; H, 4.84%. Calcd for $C_{35}H_{33}O_2F_3P_2Pd$: C, 59.13; H, 4.68. Mp 94.5—96.0 °C (decomp).

4d (R = Ph, Y = NO$_2$): Yellow powder (67%). ^{1}H NMR (270 MHz, toluene-d_8, −20 °C) δ = 1.08 (d, 0.50H, $^3J_{PH}$ = 9.89 Hz, P*Me*$_3$ of *cis*-**4d**), 1.31 (d, 0.50H, $^3J_{PH}$ = 8.06 Hz, P*Me*$_3$ of *cis*-**4d**), 1.62 (t, 5.00H, J = 3.30 Hz, virtual coupling, P*Me*$_3$ of *trans*-**4d**), 2.48 (t, 1.63H, $^3J_{PH}$ = 7.14 Hz, C*H*$_2$Ph of *trans*-**4d**), 3.14 (dd, 0.37H, $^3J_{PH}$ = 10.8, 3.48 Hz, C*H*$_2$Ph of *cis*-**4d**), 6.20—7.90 (m, 24H, aromatic H); ^{13}C{^{1}H} NMR (101 MHz, toluene-d_8, −20 °C, only signals of *trans*-**4d** was obtained) δ = 11.5 (t, J = 13.9 Hz, virtual coupling, P*Me*$_3$), 14.4 (br. s, *C*H$_2$C$_6$H$_4$-4-NO$_2$), 117.2 (q, $^1J_{FC}$ = 291.7 Hz, OCO*C*F$_3$), 122.6 (s), 130.6 (s), 144.6 (s), 154.8 (s, CH$_2$*C*$_6$H$_4$-4-NO$_2$), 128.8 (overlapped with the signal of toluene-d_8), 131.4 (s), 133.0 (t, J_{PC} = 10.3 Hz, virtual coupling), 133.1 (t, J_{PC} = 6.36 Hz, virtual coupling, PMe*Ph*$_2$), 161.2 (q, $^2J_{FC}$ = 35.8 Hz, O*C*OCF$_3$); ^{19}F NMR (254 MHz, CD$_2$Cl$_2$, −20 °C) δ = −73.9 (s, 0.26F, *cis*-**4d**), −74.0 (s, 0.74F, *trans*-**4d**); ^{31}P{^{1}H} NMR (109 MHz, CD$_2$Cl$_2$, −20 °C) δ = 11.6 (s, 1.54P, PMe$_3$ of *trans*-**4d**), 7.49 (AB q, 0.23P, $^2J_{PP}$ = 42.6 Hz, PMe$_3$ of *cis*-**4d**), 18.5 (AB q, 0.23P, $^2J_{PP}$ = 42.6 Hz, PMe$_3$ of *cis*-**4d**); IR 1713 ($\nu_{C=O}$), 893 cm^{-1} (ν_{P-C}). Found: C, 55.37; H, 4.33; N, 1.83%. Calcd for $C_{35}H_{32}O_4NF_3P_2Pd$: C, 55.61; H, 4.27; N, 1.85%. Mp 73.5—74.5 °C (decomp).

Carbonylation of Benzyl Trifluoroacetate Catalyzed by a Palladium Complex. A DMF solution (5 cm^3) of benzyl trifluoroacetate (410 mg, 2.01 mmol), [Pd(dba)$_2$] (23 mg, 0.040 mmol), 1,3-bis(diphenylphosphino)propane (16 mg, 0.039 mmol), benzyl alcohol (0.230 cm^3, 2.23 mmol) and triethylamine (0.305 cm^3, 2.20 mmol) was placed in a 100 cm^3 stainless autoclave purged with argon. The autoclave was pressurized with carbon monoxide (7.0 MPa at room temperature) and the solution was stirred for 24 h at 100 °C. After the autoclave was cooled to room temperature, the CO pressure was released. The products were identified with GC and GC-MS by comparison with a corresponding authentic sample.

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References

1) a) J. Tsuji, "Palladium Reagents and Catalysts, Innovations in Organic Synthesis," Wiley, Chichester (1995); b) J. P. Collman, L. S. Hegedus, J. N. Norton, and R. G. Finke, "Principles and Applications of Organotransition Metal Chemistry," University Science Books, California (1987); c) R. H. Crabtree, "The Organometallic Chemistry of the Transition Metals," 2nd ed, Wiley-Interscience, New York (1994); d) A. Yamamoto, "Organotransition Metal Chemistry," Wiley-Interscience, New York (1986).

2) a) K. Khumtaveeporn and H. Alper, *Acc. Chem. Res.*, **28**, 414 (1995); b) H. E. Bryndza and W. Tam, *Chem. Rev.*, **88**, 1163 (1988); c) D. Milstein, *Acc. Chem. Res.*, **17**, 221 (1984).

3) A. Yamamoto, *Adv. Organomet. Chem.*, **34**, 111 (1992), references cited therein.

4) a) T. Yamamoto, J. Ishizu, and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, **55**, 623 (1982); b) T. Yamamoto, J. Ishizu, and A. Yamamoto, *J. Am. Chem. Soc.*, **103**, 6863 (1981); c) T. Yamamoto, J. Ishizu, T. Kohara, S. Komiya, and A. Yamamoto, *J. Am. Chem. Soc.*, **102**, 3758 (1980); d) J. Ishizu, T. Yamamoto, and A. Yamamoto, *Chem. Lett.*, **1976**, 1091.

5) T. Yamamoto, M. Akimoto, O. Saito, and A. Yamamoto, *Organometallics*, **5**, 1559 (1986).

6) a) K. Nagayama, F. Kawataka, M. Sakamoto, S. Shimizu, and A. Yamamoto, *Chem. Lett.*, **1995**, 367; b) K. Nagayama, F. Kawataka, M. Sakamoto, S. Shimizu, and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, **72**, 573 (1999).

7) K. Nagayama, I. Shimizu, and A. Yamamoto, *Chem. Lett.*, **1998**, 1143.

8) Reports on C–O bond cleavage by transition metal complexes: M. E. van der Boom, S.-Y. Liou, Y. Ben-David, L. J. W. Shimon, and D. Milstein, *J. Am. Chem. Soc.*, **120**, 6531 (1998), and references cited therein.

9) Examples of the study on C–O activation of trifluoroacetic acid esters by other transition metal complexes. Ir: A. S. Goldman and J. Halpern, *J. Am. Chem. Soc.*, **109**, 7537 (1987); Co: Y. Hayashi, T. Yamamoto, A. Yamamoto, S. Komiya, and Y. Kushi, *J. Am. Chem. Soc.*, **108**, 385 (1986).

10) F. Ozawa, T. Ito, Y. Nakamura, and A. Yamamoto, *J. Organomet. Chem.*, **168**, 375 (1979).

11) T. Ito, H. Tsuchiya, and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, **50**, 1319 (1977).

12) Synthesis and chemical properties of similar acyl(aryloxo)bis(tertiary phosphine)palladium complexes prepared by carbonylation of alkyl(aryloxo)bis(tertiary phosphine)palladium complexes have been reported: S. Komiya, Y. Akai, K. Tanaka, T. Yamamoto, and A. Yamamoto, *Organometallics*, **4**, 1130 (1985).

13) Preparation of bis(aryloxo)bis(tertiary phosphine)palladium(II) complexes by treatment of [Pd(PPh$_3$)$_4$] with phenols has been reported. a) H. A. Tayim and N. S. Akl, *J. Inorg. Nucl. Chem.*, **36**, 944 (1974), however, we could not reproduce the synthesis in our hands; b) A. S. Berenblyum, L. I. Lakhman, I. I. Moiseev, and E. D. Radchenko, *Koord. Khim.*, **2**, 845 (1976); c) P. Roffia, G. Gregorio, F. Conti, G. F. Pregaglia, and R. Ugo, *J. Mol. Catal.*, **2**, 191 (1977).

14) a) P. W. Jolly and R. Mynott, *Adv. Organomet. Chem.*, **19**, 257 (1981); b) D. A. Redfield, J. H. Nelson, and L. W. Cary, *Inorg. Nucl. Chem. Lett.*, **10**, 727 (1974); c) D. A. Redfield, L. W. Cary, and J. H. Nelson, *Inorg. Chem.*, **14**, 50 (1975).

15) D. A. Redfield and J. H. Nelson, *Inorg. Chem.*, **12**, 15 (1973).

16) Similar carbonylation of benzyl carboxylates by a palladium complex has been reported: J. M. Baird, J. R. Kern, G. R. Lee, D. J. Morgans, Jr., and M. L. Sparacino, *J. Org. Chem.*, **56**, 1928 (1991).

17) Y.-S. Lin and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, **71**, 723 (1998); Y.-S. Lin and A. Yamamoto, *Organometallics*, **17**, 3466 (1998).