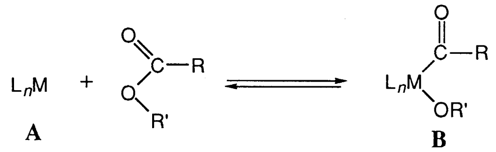
Preparation and Reactivities of Acyl(carboxylato)palladium Complexes

Kazuhiro Nagayama, Futoshi Kawataka, Masato Sakamoto, Isao Shimizu, and Akio Yamamoto*
Department of Applied Chemistry, School of Science and Engineering, Waseda University, 3-4-1 Ohkubo, Shinjuku-ku, Tokyo 169

(Received January 24, 1995)

Acyclic acid anhydrides oxidatively add to Pd(styrene)$(PMe_3)_2$ with C-O bond cleavage to give corresponding acyl(carboxylato)palladium(II) complexes **3a**-**3e** that are isolated and identified. The acetato ligand in **3a** is exchanged with added acetic acid. Treatment of **3a** with formic acid at room temperature yields acetaldehyde, acetic acid and CO_2. Reaction of **3a** with dihydrogen liberates acetaldehyde, acetic acid and ethanol. Catalytic hydrogenolysis of octanoic and benzoic anhydrides into aldehydes and carboxylic acids was found to be catalyzed by $Pd(PPh_3)_4$

In contrast to the abundance of synthetic methods utilizing oxidative addition process of organic halides involving the carbon-halogen bond cleavage, successful application of the metal-catalyzed C-O bond cleavage process to organic synthesis is still limited except for the synthesis utilizing the palladium-promoted allyl-O bond cleavage.[1] The synthetic application of the C-O bond cleavage may have been hampered by the scarcity of the known examples of oxidative addition of esters, anhydrides and ethers to low valent transition metal complexes to form metal-carbon and metal oxygen bonds (Eq. 1).

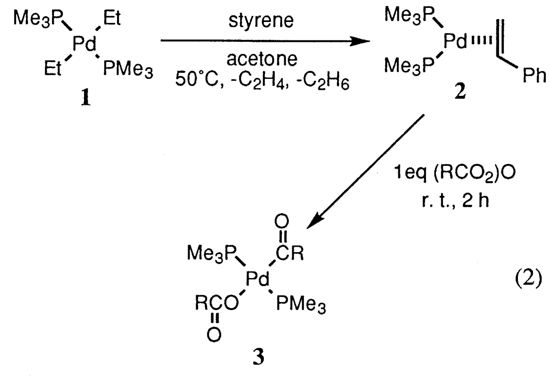


(1)

We have previously reported examples of oxidative addition of aryl carboxylates[2] and acid anhydrides[3,4] to Ni(0) complexes to form complexes of type **B** as well as its reverse process to cause C-O bond formation.[5] However, because of the high affinity of the Ni(0) complexes for CO formed by decarbonylation of the acylnickel species, the Ni(0) complexes tend to form CO-bound nickel complexes that are inert to furthur reactions.[6] We now report the first example of the oxidative addition of acyclic acid anhydrides to a Pd(0) complex and utilization of the C-O bond cleavage process to organic synthesis with a palladium catalyst.

A coordinatively unsaturated complex **2**[7] that can be readily derived by thermolysis of the diethylpalladium complex **1** reacts with various acyclic acid anhydrides to give acyl(carboxylato)palladium(II) complexes, **3a**-**3e**. As a typical example, a solution of **2** which was generated *in situ* at 50 °C from **1** in the presence of styrene (1.5 eq) in dry acetone under an argon atmosphere was treated at 25 °C with an equivalent of acetic anhydride. The mixture was stirred for 0.5 h and dried *in vacuo*. The white residue was washed with a small amount of Et_2O and recrystallized from Et_2O as white crystals. Complexes **3a** (yield 68%), **3b** (53 %), **3c** (17%), **3d** (53%) and **3e** (67%) were also prepared similarly. These complexes have been identified with spectroscopic means and elemental analysis.[8]

The acetato ligand in **3a** interacts with free acetic acid and its fast exchange with the added carboxylic acid is observed at 25 °C by ^1H NMR.[9]

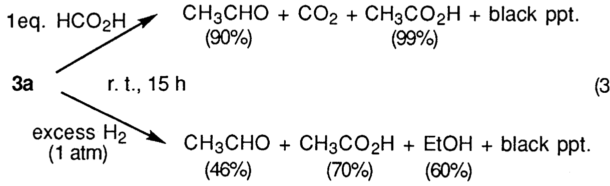


(2)

(**3a** : R = Me , **3b** : R = Et ,**3c** : R = ^{i}Pr ,**3d** : R= ^{t}Bu , **3e** : R= Ph)

Treatment of **3a** with formic acid at -30 °C gives an unstable, intermediate acetylpalladium formate complex by the exchange of the acetato ligand with formic acid as evidenced by the ^1H NMR observation.[10] When the reaction of **3a** with an equivalent of formic acid was carried out at room temperature for 15 h, decomposition of the acetylpalladium formate intermediate occurred to give a black precipitate of Pd(0) with formation of ca. 1 equivalent each of acetaldehyde and acetic acid as comfirmed by gas chromatography and mass spectroscopy together with CO_2. Formation of these products may be accounted for by decarboxylation of the intermediate acetylpalladium formate to give an acetylpalladium hydride that liberates acetaldehyde.

The acetyl(acetato)palladium(II) complex **3a** reacts with H_2 to undergo the hydrogenolysis of the acetato and acyl ligands liberating acetaldehyde, acetic acid and ethanol in yields shown in Eq. 3.[11] Ethanol may have been produced by reduction of acetaldehyde.[12]



(3)

Extension of the finding of the stoichiometric hydrogenation of **3a** led to development of a novel palladium-catalyzed process as shown in Eq. 4.[13] Acid anhydrides (octanoic and benzoic) were hydrogenated quantitatively into corresponding aldehydes and acids in the presence of $Pd(PPh_3)_4$ (1 mol%).

$$(RCO)_2O \xrightarrow[\text{THF, 80 °C, 15 h}]{Pd(PPh_3)_4,\ H_2} RCHO + RCOOH \quad (R = C_7H_{15}, Ph) \tag{4}$$

This study was supported by a grant from Nippon Zeon Co. and the Grant-in-Aid for Scientific Research on Priority Area of Reactive Organometallics No. 05236106 from the Ministry of Education, Science and Culture, Japan.

References and Notes

1 A. Yamamoto, *Adv. Organometal. Chem.* **34**, 111 (1992).

2 T. Yamamoto, J. Ishizu, T. Kohara, S. Komiya, and A. Yamamoto, *J. Am. Chem. Soc.* **102**, 3758 (1980).

3 S. Komiya, A. Yamamoto, and T. Yamamoto, *Chem. Lett.*, 193 (1981).

4 K. Sano, T. Yamamoto, and A. Yamamoto, *Chem. Lett.*, 115 (1983).

5 S. Komiya, Y. Akai, K. Tanaka, T. Yamamoto, and A. Yamamoto, *Organometallics* **4**, 1130 (1985).

6 A. M. Castãno, and A. M. Echavarren, *Organometallics* **13**, 2262 (1994).

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

8 Melting points, NMR, IR and elemental analysis data for **3a**-**3e** are as follows. Melting points were measured in argon atmosphere. All NMR spectra were observed in acetone-d_6 solutions at 25 °C, chemical shift values of $^{31}P\{^1H\}$ NMR are ppm from 85%-H_3PO_4, and all IR spectra were measured in KBr pellets. **3a** : mp 69-71 °C dec.; ^1H NMR (90 MHz): δ 1.30 (virtual triplet, 18H, *J* = 3.7 Hz), 1.70 (s, 3H), 2.27 (brs, 3H); $^{31}P\{^1H\}$ NMR (161.8 MHz): δ -19.2 (s); $^{13}C\{^1H\}$ NMR (100.5 MHz): δ 237.2, 175.9, 42.0, 24.9, 14.2; IR (cm^{-1}): 1676 ($\nu_{C=O}$), 1572 ($\nu_{C(=O)O}$), 950 (ν_{P-C}). Found : C, 33.4 ; H 7.1%. Calcd for $C_{10}H_{24}O_3P_2Pd$: C, 33.3 ; H, 6.7%. **3b** : mp 75-78 °C dec.; ^1H NMR (90 MHz): δ 0.88 (t, 3H, *J* = 7.7 Hz), 0.91 (t, 3H, *J* = 7.7 Hz), 1.28 (vt, 18H, *J* = 3.7 Hz), 1.96 (q, 2H, *J* = 7.7 Hz), 2.58 (q, 2H, *J* = 7.7 Hz); $^{31}P\{^1H\}$ NMR (161.8 MHz): δ -23.5 (s); $^{13}C\{^1H\}$ NMR (100.5 MHz): δ 239.6, 179.0, 49.2, 31.2, 14.5, 12.0, 9.5; IR (cm^{-1}): 1662 ($\nu_{C=O}$), 1566 ($\nu_{C(=O)O}$), 956 (ν_{P-C}). Found : C, 37.2 ; H 7.8%. Calcd for $C_{12}H_{28}O_3P_2Pd$: C, 37.1 ; H, 7.3%. **3c** : mp 76-79 °C dec.; ^1H NMR (400 MHz): δ 1.00 (d, 6H, *J* = 7.3 Hz), 1.24 (d, 6H, *J* = 7.3 Hz), 1.28 (vt, 18H, *J* = 3.7 Hz), 2.18-2.29 (m, 2H); $^{31}P\{^1H\}$ NMR (109.4 MHz): δ -13.6 (s); $^{13}C\{^1H\}$ NMR (100.5 MHz); δ 243.3, 181.9, 52.7, 37.9, 21.5, 19.3, 14.8; IR (cm^{-1}): 1650 ($\nu_{C=O}$), 1550 ($\nu_{C(=O)O}$), 954 (ν_{P-C}). Found : C, 40.4 ; H 8.1%. Calcd for $C_{14}H_{32}O_3P_2Pd$: C, 40.4 ; H, 7.7%. **3d** : mp 104-106 °C dec.; ^1H NMR (90 MHz): δ 1.06 (s, 9H), 1.17 (s, 9H), 1.31 (vt, *J* = 3.9 Hz): $^{31}P\{^1H\}$ NMR (109.4 MHz): δ -14.6 (s); $^{13}C\{^1H\}$ NMR (67.9 MHz); δ 245.8, 183.2, 54.3, 40.5, 28.4, 15.3; IR (cm^{-1}): 1644 ($\nu_{C=O}$), 1546 ($\nu_{C(=O)O}$), 954 (ν_{P-C}). Found : C, 43.6 ; H 8.6%. Calcd for $C_{16}H_{36}O_3P_2Pd$: C, 43.2 ; H, 8.1%. **3e** : mp 123-125 °C dec.; ^1H NMR (90 MHz): δ 1.17 (vt, 18H, *J* = 3.7Hz), 7.3-7.4 (m, 3H), 7.5-7.6 (m, 3H), 7.9-8.1 (m, 2H), 8.2-8.3 (m, 2H); $^{31}P\{^1H\}$ NMR (161.8 MHz): δ -19.3 (s); $^{13}C\{^1H\}$ NMR (100.5 MHz): δ 233.3, 172.0, 143.7, 139.8, 133.2, 130.7, 130.6, 130.4, 129.8, 129.7, 13.9; IR (cm^{-1}): 1638 ($\nu_{C=O}$), 1558 ($\nu_{C(=O)O}$), 952 (ν_{P-C}). Found : C, 49.5 ; H 5.9%. Calcd for $C_{20}H_{28}O_3P_2Pd$: C, 49.6 ; H, 5.8%.

9 The ^1H chemical shift (90 MHz) of the acetate signal of **3a** is shifted upon addition of the increasing amounts of acetic acid (as shown in the parentheses) towards lower magnetic field as follows; δ 1.69 (0), 1.83 (0.5), 1.86 (1.0), 1.89 (2.0), 1.92 (4.0), 1.94 (8.0), 1.95 (16), 1.95 (free AcOH).

10 The ^1H chemical shift (90 MHz) of the acetate signal of **3a** and that of formate of formic acid are shifted upon addition of the increasing amounts of formic acid (as shown in the parentheses) towards lower and higher magnetic fields, respectively, as follows; δ 1.68 (0); 1.84, 8.28 (0.5); 1.91, 8.29 (1.0); 1.94, 8.25 (2.0); 1.95, 8.20 (4.0); 1.96, 8.16 (8.0); 1.95, 8.12 (free AcOH and free HCOOH).

11 B. T. Heaton, S. P. A. Hébert, J. A. Iggo, F. Metz, R. Whyman, *J. Chem. Soc. Dalton Trans.* 3081 (1993).

12 H. Musso, K. Figge, *Chem. Ber.* **95**, 1844 (1962).

13 The corresponding cobalt-catalyzed hydrogenation of carboxylic anhydrides have been reported; H. Wakamatsu, J. Furukawa, N. Yamakami, *Bull. Chem. Soc. Jpn.* **44**, 288 (1971).