

## Insertion of Carbon Monoxide into a Palladium–Allyl Bond

Fumiyuki Ozawa,\* Tae-il Son, Kohtarō Osakada, and Akio Yamamoto\*

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 227, Japan

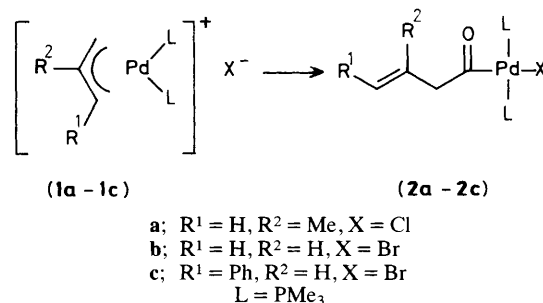
Trimethylphosphine-co-ordinated  $\pi$ -allylpalladium complexes  $[(\pi\text{-allyl})\text{Pd}(\text{PMe}_3)_2]\text{X}$  ( $\text{X} = \text{halide}$ ) undergo CO insertion into the palladium–allyl bond to give 3-butenoylpalladium complexes under mild conditions.

Despite wide usage of palladium-catalysed carbonylation of allylic compounds, efficient catalysis that proceeds under low CO pressure is still limited.<sup>1</sup> Since catalytic carbonylation reactions generally involve CO insertion into a metal–carbon bond to give an acyl intermediate, the general requirement of high CO pressure in the palladium-catalysed carbonylation of allylic compounds should be attributed predominantly to difficulty of CO insertion into a palladium–allyl bond which is stabilised by  $\pi$ -bonding.<sup>†</sup> Indeed there is no precedent of CO insertion into an isolated  $\pi$ -allylpalladium complex.<sup>‡</sup> We report CO insertion under mild conditions into isolated  $\pi$ -allylpalladium complexes co-ordinated with  $\text{PMe}_3$  ligands.

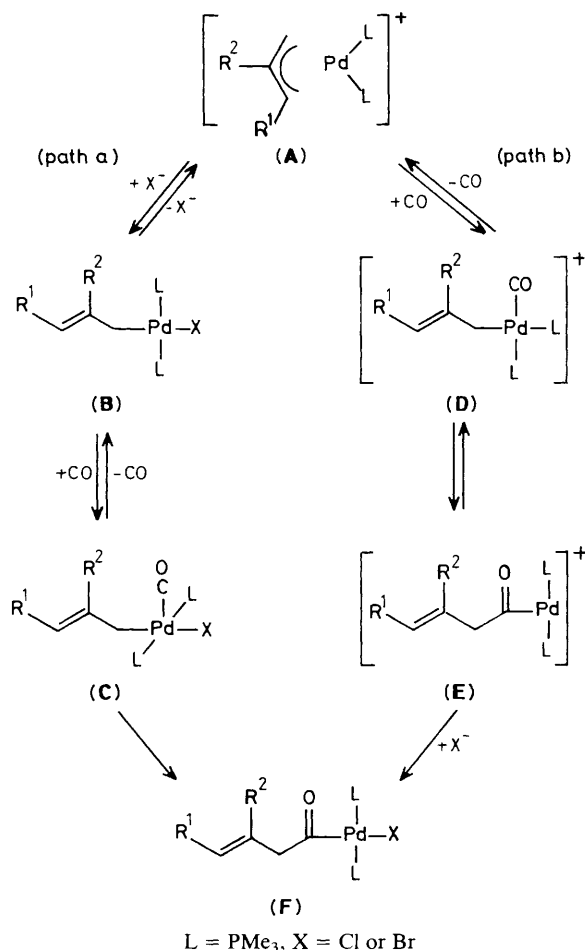
Cationic  $(\pi\text{-allyl})\text{bis}(\text{trimethylphosphine})\text{palladium}(\text{II})$  complexes with halides as counter anions (**1a–1c**)<sup>§</sup> react with carbon monoxide in  $\text{CH}_2\text{Cl}_2$  at room temperature to give the corresponding 3-butenoylpalladium halide complexes (**2a–2c**, respectively), which have been isolated as white (**2a**) and yellow (**2b** and **2c**) crystalline solids and characterised by means of i.r. and n.m.r. spectroscopy and elemental analysis (Scheme 1).<sup>¶</sup> The reactions of (**1a**) and (**1b**) are accomplished within several hours under an atmospheric pressure of CO, whereas that of (**1c**) does not proceed under the same reaction conditions but is completed under 10 atm of CO within 4 h at room temperature.

The CO insertion reaction is affected markedly by the number and type of tertiary phosphine ligand (L). In contrast to the facile CO insertion into the Pd–allyl bond in (**1a**) co-ordinated with two  $\text{PMe}_3$  ligands,  $(\eta^3\text{-2-MeC}_3\text{H}_4)\text{Pd}(\text{Cl})(\text{PMe}_3)$  with one  $\text{PMe}_3$  ligand is totally

inactive towards CO insertion even under pressurised conditions. The  $\text{PMePh}_2$ -co-ordinated complex  $[(\eta^3\text{-C}_3\text{H}_5)\text{Pd}(\text{PMePh}_2)_2]\text{Br}$  (**1d**) reacts with carbon monoxide (10 atm) in  $\text{CH}_2\text{Cl}_2$  at room temperature to give the corresponding CO insertion product *trans*- $\text{Pd}(\text{COCH}_2\text{CH}=\text{CH}_2)(\text{Br})$ –



Scheme 1. Reagents and conditions: CO, room temp.



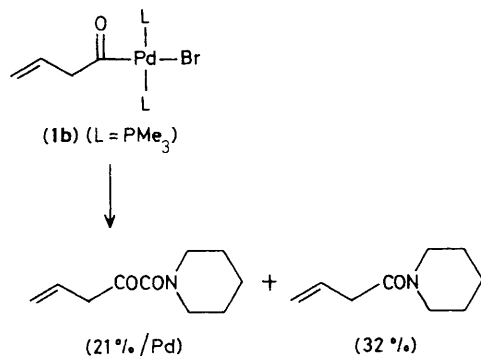
Scheme 2

<sup>†</sup> An alternative mechanism which does not involve CO insertion into a palladium–allyl bond but proceeds through nucleophilic attack on a co-ordinated CO ligand has been proposed for carbonylation of isolated  $\pi$ -allylpalladium complexes with alcohols to give 3-butenic acid esters.<sup>2</sup>

<sup>‡</sup> It has been reported very recently that reaction of  $\text{Pd}(\text{CO})(\text{PPh}_3)_3$  with cinnamyl bromide under CO pressure gives 4-phenyl-3-butenoylpalladium bromide complex.<sup>3</sup> This report provides indirect evidence for CO insertion into a  $\pi$ -allylpalladium complex.

<sup>§</sup> Complexes (**1a–1c**) have been prepared by reactions of  $\text{Pd}(\text{styrene})(\text{PMe}_3)_2$  with allyl halides and were characterised by means of i.r. and n.m.r. spectroscopy and elemental analysis.

<sup>¶</sup> *Spectroscopic data for (2a):* <sup>1</sup>H n.m.r. ( $\text{CD}_2\text{Cl}_2$ ,  $-40^\circ\text{C}$ ),  $\delta$  4.88 [1H, s,  $\text{CH}(\text{H})=\text{C}$ ], 4.72 [1H, s,  $\text{CH}(\text{H})=\text{C}$ ], 3.38 (2H, s,  $\text{CH}_2\text{CO}$ ), 1.80 (3H, s,  $\text{C}=\text{CMe}$ ), 1.38 (18H, t,  $J$  4 Hz,  $\text{PMe}$ ); <sup>13</sup>C{<sup>1</sup>H} n.m.r. ( $\text{CD}_2\text{Cl}_2$ ,  $-40^\circ\text{C}$ ),  $\delta$  236.4 (s,  $\text{C}=\text{O}$ ), 139.2 (s,  $\text{CH}_2=\text{CMe}$ ), 115.0 (s,  $\text{CH}_2=\text{C}$ ), 64.8 (t,  $J$  16 Hz,  $\text{CH}_2\text{CO}$ ), 23.5 (s,  $\text{CH}_2=\text{CMe}$ ), 14.1 (t,  $J$  14 Hz,  $\text{PMe}$ ); i.r. (KBr) 1650  $\text{cm}^{-1}$  ( $\text{C}=\text{O}$ ); (**2b**) <sup>1</sup>H n.m.r. ( $\text{CD}_2\text{Cl}_2$ ,  $-40^\circ\text{C}$ ),  $\delta$  6.28 (1H, m,  $\text{CH}_2=\text{CH}$ ), 5.26 [1H, d,  $J$  17 Hz,  $\text{CH}(\text{H})=\text{C}$ ], 5.16 [1H, d,  $J$  10 Hz,  $\text{CH}(\text{H})=\text{C}$ ], 3.32 (2H, d,  $J$  7 Hz,  $\text{CH}_2\text{CO}$ ), 1.48 (18H, t,  $J$  4 Hz,  $\text{PMe}$ ); <sup>13</sup>C{<sup>1</sup>H} n.m.r. ( $\text{CD}_2\text{Cl}_2$ ,  $-40^\circ\text{C}$ ),  $\delta$  240.3 (s,  $\text{C}=\text{O}$ ), 131.2 (s,  $\text{CH}_2=\text{CH}$ ), 118.6 (s,  $\text{CH}_2=\text{CH}$ ), 59.6 (t,  $J$  15 Hz,  $\text{CH}_2\text{CO}$ ), 14.8 (t,  $J$  14 Hz,  $\text{PMe}$ ); i.r. (KBr) 1668  $\text{cm}^{-1}$  ( $\text{C}=\text{O}$ ); (**2c**) <sup>1</sup>H n.m.r. ( $\text{CD}_2\text{Cl}_2$ ,  $-40^\circ\text{C}$ ),  $\delta$  7.33 (5H, m, Ph), 6.60 (1H, dt,  $\text{PhCH}=\text{CH}$ ), 6.45 (1H, d,  $J$  16 Hz,  $\text{PhCH}=\text{CH}$ ), 3.38 (2H, d,  $J$  7 Hz,  $\text{CH}_2\text{CO}$ ), 1.44 (18H, t,  $J$  4 Hz,  $\text{PMe}$ ); <sup>13</sup>C{<sup>1</sup>H} n.m.r. ( $\text{CD}_2\text{Cl}_2$ ,  $-40^\circ\text{C}$ ),  $\delta$  238.8 (s,  $\text{C}=\text{O}$ ), 136.6 (s,  $\text{PhCH}=\text{CH}$ ), 122.6 (s,  $\text{PhCH}=\text{CH}$ ), 59.4 (t,  $J$  16 Hz,  $\text{CH}_2\text{CO}$ ), 15.1 (t,  $J$  14 Hz,  $\text{PMe}$ ); i.r. (KBr) 1650  $\text{cm}^{-1}$  ( $\text{C}=\text{O}$ ).



**Scheme 3.** Reagents and conditions: CO (50 atm), C<sub>5</sub>H<sub>10</sub>NH (10 equiv./Pd), toluene, 50 °C.

(PMePh<sub>2</sub>)<sub>2</sub> (**2d**) which has been obtained as a mixture with the starting complex (**1d**) as confirmed by i.r. spectroscopy [ $\nu(\text{CO})$  1663 cm<sup>-1</sup>]. Complex (**2d**) is unstable in the solid state as well as in solution in the absence of free CO and readily undergoes decarbonylation at room temperature to give the  $\pi$ -allyl complex (**1d**). The PMe<sub>3</sub>-co-ordinated 3-butenoyl complex (**2b**), on the other hand, is much more stable towards decarbonylation than (**2d**), and it takes *ca.* 12 h at 60 °C to complete the decarbonylation to afford (**1b**).

The nature of the counter anion in the  $\pi$ -allyl complexes also influences the CO insertion reaction. Thus the cationic  $\pi$ -allylpalladium complex with the BF<sub>4</sub><sup>-</sup> anion [ $(\eta^3\text{-C}_3\text{H}_5)\text{-Pd}(\text{PMe}_3)_2\text{BF}_4$ ] does not undergo CO insertion under 20 atm of CO at room temperature in 1 day. Furthermore, treatment of (**2b**) with AgBF<sub>4</sub> in CD<sub>2</sub>Cl<sub>2</sub> at room temperature results in rapid decarbonylation to give [ $(\eta^3\text{-C}_3\text{H}_5)\text{Pd}(\text{PMe}_3)_2\text{BF}_4$ ], quantitatively, as confirmed by n.m.r. spectroscopy.

Two mechanisms are conceivable for the CO insertion (Scheme 2). The cationic  $\pi$ -allylpalladium complex (**A**) undergoes co-ordination of the halide to give a four-co-ordinated  $\sigma$ -allylpalladium complex (**B**). Co-ordination of CO to (**B**) is followed by migration of the allyl group on the bound carbonyl ligand to afford the 3-butenoylpalladium complex (**F**) (path a). Among these processes, occurrence of the

interconversion between (**A**) and (**B**) has been confirmed by n.m.r. spectroscopy. The other mechanism (path b) involves the four-co-ordinated cationic  $\sigma$ -allylpalladium carbonyl intermediate (**D**) which is formed by CO co-ordination to (**A**). Migration of the allyl group on the CO ligand in (**D**) affords a co-ordinatively unsaturated 3-butenoyl complex (**E**) which undergoes subsequent co-ordination of halide anion to give (**F**). Further mechanistic studies are in progress.

The present results indicate that the CO insertion into a palladium-allyl bond is a kinetically feasible process, and it can be operative under the conditions that stabilise the CO insertion product. Blocking the co-ordination site required for decarbonylation of the insertion product is of particular importance for promoting the CO insertion.

The CO insertion into palladium-allyl bonds has enabled us to achieve stoichiometric double carbonylation of allylic compounds. Reaction of (**1b**) with piperidine under CO pressure produces the  $\alpha$ -keto amide together with the amide (Scheme 3). Attempts for catalytic double carbonylation of allylic compounds are now under investigation.

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