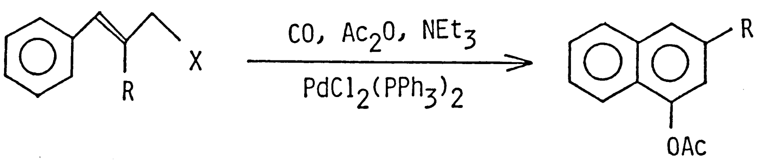
CHEMISTRY LETTERS, pp. 377-380, 1988.

Preparation and Reactivities of trans-[(E-$PhCH=CHCH_2CO)MBr(PPh_3)_2$] (M = Pd, Pt) as Key Intermediates for Cyclocarbonylation of Cinnamyl Compounds[1)]

Hiroyuki MATSUZAKA, Yoshitaka HIROE, Masakazu IWASAKI, Youichi ISHII,
Yukio KOYASU, and Masanobu HIDAI*
Department of Synthetic Chemistry, Faculty of Engineering,
The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

Reaction of $Pd(CO)(PPh_3)_3$ with trans- or cis-cinnamyl bromide under 20 atom of CO at room temperature gave trans-[(E-$PhCH=CHCH_2CO)Pd$-$Br(PPh_3)_2$] (**1**), whereas similar reaction under 1 atom of CO afforded (η^3-1-Ph-allyl)$PdBr(PPh_3)$ which was not converted into **1** under 20 atom of CO at room temperature. Very facile migration of the carbon-carbon double bond in **1** was observed in solution at ambient temperature. Treatment of **1** or its platinum analogue (**1'**) with Ac_2O and Et_3N under 60 atm of CO at 160°C gave 1-naphthyl acetate in moderate yield.

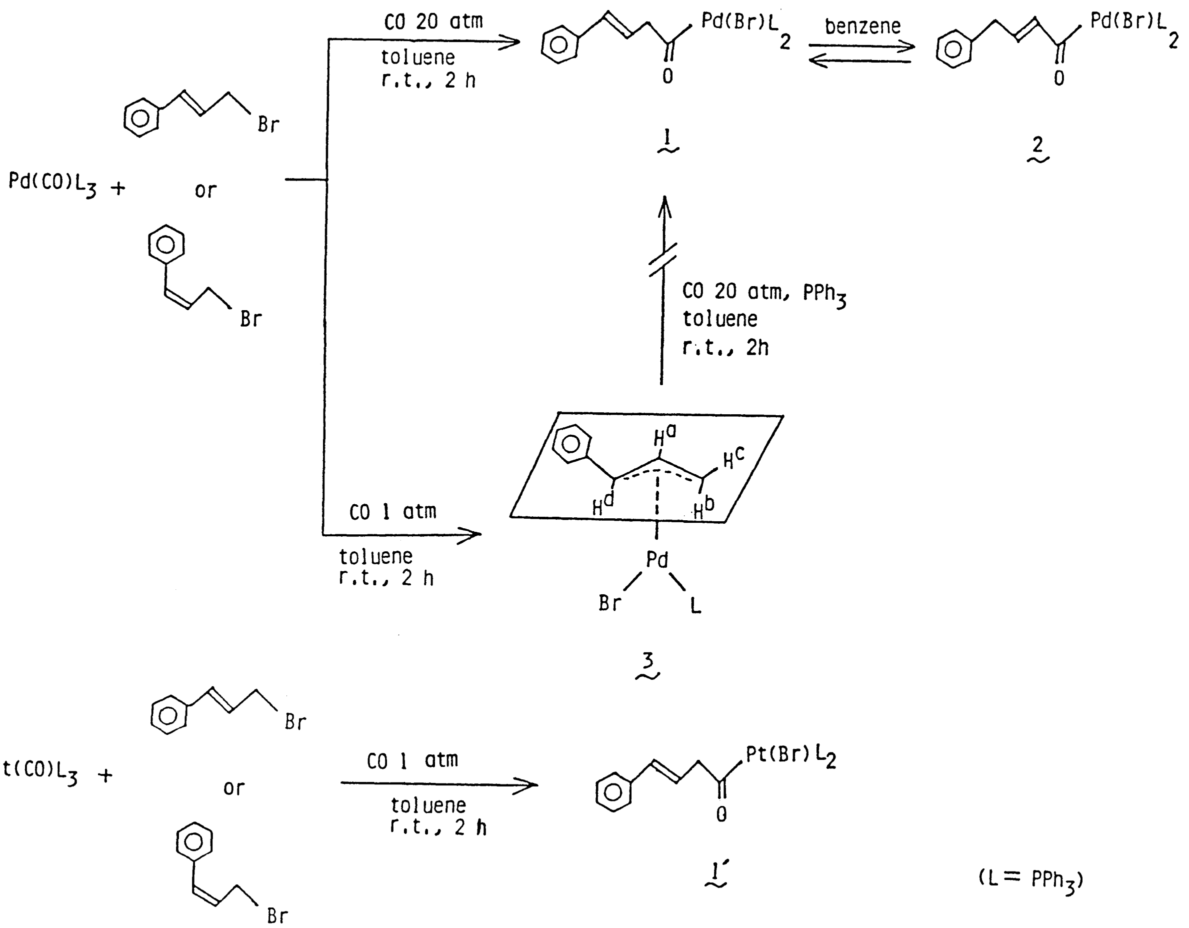
Polycyclic compounds have been receiving much attention in organic and bioorganic chemistry. Several synthetic methods have been developed by using cyclocarbonylation reactions, which include the syntheses of anthraquinone from benzophenone with $PdCl_2$,[2)] indanones from benzene and polyfunctional halides with $AlCl_3$,[3)] an indanone from tetraphenylbutatriene with $Co_2(CO)_8$,[4)] and indenones from benzene and diphenylacetylene with $Rh_4(CO)_{12}$.[5)] During the course of our studies on transition metal catalysed carbonylation reactions,[6-8)] we have recently developed a novel method for synthesis of 1-naphthol derivatives using palladium catalysed cyclocarbonylation of cinnamyl compounds (Eq.1).[9)] In order to elucidate the reaction mechanism, we have now investigated the reaction of $M(CO)(PPh_3)_3$ (M=Pd or Pt) with trans- or cis-cinnamyl bromide.



(1)

a ; R = H, X = OAc c ; R = H, X = Br
b ; R = Me, X = OAc

Reaction of $Pd(CO)(PPh_3)_3$ with trans-cinnamyl bromide in toluene at room temperature <u>under 20 atm of CO</u> gave an acyl complex trans-[(E-$PhCH=CHCH_2CO)PdBr$-$(PPh_3)_2$] (**1**) as yellow cubic crystals in 74% yield after adding hexane to the concentrated reaction mixture (Scheme 1).[10)] The IR spectrum of **1** in a KBr disk exhibits absorptions at 1667 and 1640 cm^{-1}, which are assignable to ν(CO) and ν(C=C), respectively. The platinum analogue trans-[(E-$PhCH=CHCH_2CO)PtBr(PPh_3)_2$] (**1'**) was obtained in 78% yield by similar reaction of $Pt(CO)(PPh_3)_3$ under 1 atom



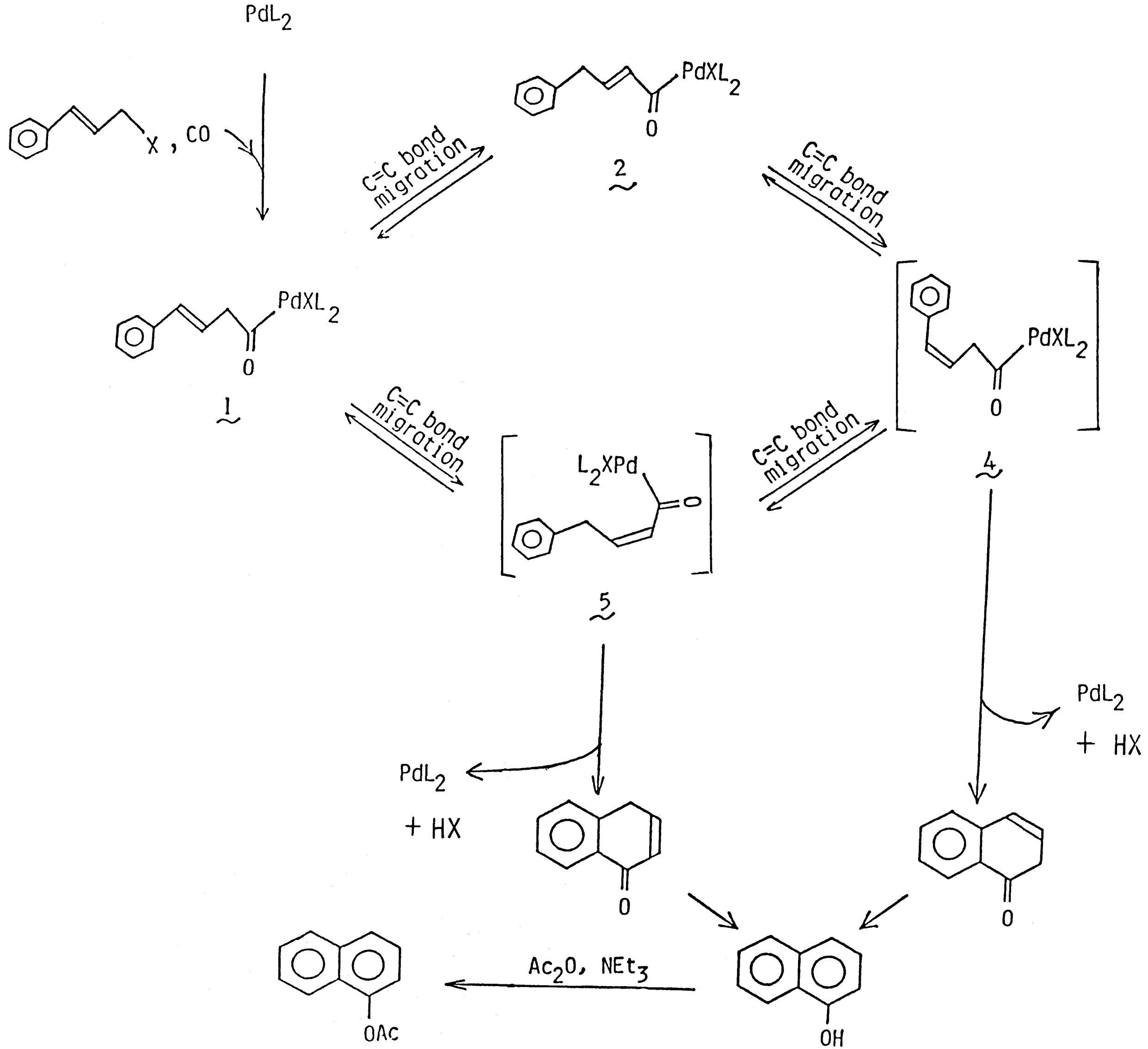
Scheme 1.

of CO11). Complex (**1'**) shows absorptions at 1660 and 1635 cm^{-1} assignable to ν(CO) and ν(C=C), respectively, in its IR spectrum. The ^{1}H NMR spectrum of **1** in C_6D_6 indicates that **1**12) rapidly isomerizes in solution to form an equilibrium mixture of **1** and *trans*-[(E-PhCH$_2$CH=CHCO)PdBr(PPh$_3$)$_2$] (**2**)13) in the ratio of 1:1 at room temperature. Complex (**2**) is supposed to be formed by carbon-carbon double bond migration in **1**, however such migration in **1'** was not observed in its ^{1}H NMR spectrum.14)

Interestingly, when Pd(CO)(PPh$_3$)$_3$ was treated with *trans*-cinnamyl bromide *under 1 atom of CO*, a π-allyl complex (η^3-1-Ph-allyl)Pd(Br)(PPh$_3$) (**3**) precipitated during the reaction, which was recrystallized from CHCl$_3$-hexane to give yellow cubic crystals in 83% yield (Scheme 1).15) This forms a sharp contrast to that the reaction of Pd(CO)(PPh$_3$)$_3$ and allyl bromide under 1 atom of CO results in the formation of a mixture of 2- and 3-butenoyl complexes.16) Furthermore, **3** was not carbonylated to give **1** at room temperature in the presence of 1 molar equiv of PPh$_3$ under 20 atom of CO. This suggests that, in the reaction of Pd(CO)(PPh$_3$)$_3$ with cinnamyl bromide under high CO pressure at room temperature, CO insertion into the palladium-carbon bond of the first formed σ-allyl complex rapidly occurs before the σ-π equilibrium is attained.

It should be noted that, on treatment of Pd(CO)(PPh$_3$)$_3$ with *cis*-cinnamyl bromide under 20 atom of CO, **1** was isolated in 70% yield, instead of the expected acyl complex, *trans*-[(Z-PhCH=CHCH$_2$CO)Pd(Br)(PPh$_3$)$_2$] (4). It may be reasonable to conclude that **4** initially formed isomerized to **1** by the carbon-carbon double bond migration as shown in Scheme 2, because carbonylation of the σ-allyl complex proceeds smoothly under high CO pressure before the σ-π equilibrium is attained as mentioned above. At room temperature, the equilibrium among acyl complexes **1**, **2**, **4**, and **5** lies so far to **1** and **2** which have probably the more sterically favorable structures.

Reactivities of above acyl complexes were examined under catalytic cyclocarbonylation conditions. Treatment of **1** or **1'** with excess Ac_2O and Et_3N under 60 atom of CO at 160 °C gave 1-naphthyl acetate in 54, or 40% yield, respectively.



Scheme 2.

This reaction is thought to proceed through acyl complexes 4 and/or 5, which arise from carbon-carbon double bond migration in 1. Intramolecular cyclization of 4 and/or 5 results in the formation of 2H- and/or 4H-naphthalenones, which isomerize to 1-naphthol and are then acetylated by Ac_2O and Et_3N. Furthermore, complex 1 showed a similar catalytic activity to $PdCl_2(PPh_3)_2$ for cyclocarbonylation of cinnamyl bromide.

In conclusion, palladium catalysed cyclocarbonylation of cinnamyl compounds (Eq.1) is supposed to proceed according to the following mechanism. The first step is oxidative addition of cinnamyl compounds to palladium(0) species to afford a σ-allyl complex, which is carbonylated smoothly to form 1.[17] Carbon-carbon double bond migration in 1 might provide 4 or 5, which is followed by intramolecular cyclization to give 1-naphthyl acetate and regenerate palladium(0) species (Scheme 2).

References

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10) Found: C,65.27; H,5.04; Br,8.84%. Calcd for $C_{46}H_{39}BrOP_2Pd\cdot 1/2$toluene : C,65.82; H,4.92; Br,9.25%. ^{31}P NMR(C_6D_6) 18.46(s).
11) Found: C,60.75; H,4.60; Br,8.43%. Calcd for $C_{46}H_{39}BrOP_2Pt\cdot 1/2$toluene C,59.98; H,4.38; Br,8.06%. ^{31}P NMR(C_6D_6) 18.45(s). Satellite peaks were also observed(J_{Pt-P} = 3486 Hz).
12) ^1H NMR(C_6D_6) 2.77(d, J=9.0 Hz, 2H), 5.83(d, J=16.2 Hz, 1H), 6.40(dt, 1H).
13) ^1H NMR(C_6D_6) 2.89(d, J=9.2 Hz, 2H), 5.09(d, J=13.7 Hz, 1H), 5.55(dt, 1H).
14) ^1H NMR(C_6D_6) 2.38(d, J=7.3 Hz, 2H), 5.70(d, J=15.9 Hz, 1H), 6.33(td, 1H).
15) Found: C,57,85; H,4.34; Br,14.50%. Calcd for $C_{27}H_{24}BrPPd$: C,57.31; H,4.28; Br,14.12%. ^1H NMR($CDCl_3$) 5.90(m, H^a), 5.06(d, J=22.9 Hz, H^b), 5.06(d, J=7.6 Hz, H^c), 6.72(dd, J=15.7, 5.7 Hz, H^d).
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17) An alternative path involving carbonylation of a σ-Z-allyl complex generated by syn-anti and π-σ isomerization of 3 cannot be excluded, although a path including prior formation of 1 instead of 3 appears to be a more favorable.

(Received November 26, 1987)