Insertion of Alkenes into a Palladium–Acetyl Bond

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A cationic acetylpalladium(II) complex *cis*-$[Pd(COMe)(NCMe)(dppe)]^+BF_4^-$ **2** exhibits extremely high reactivity toward simple alkenes including cyclopentene, cycloheptene and methyl acrylate to give the corresponding alkene-inserted complexes, which have been characterised by IR and NMR spectroscopy.

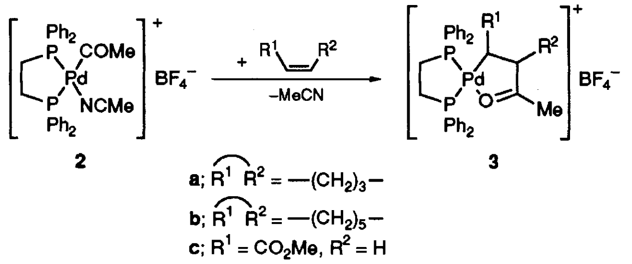
Insertion of alkenes into a palladium–carbon bond is assumed to be a crucial process in many palladium-catalysed organic reactions.[1] However, it is generally difficult to directly observe this process by using an isolated organopalladium complex,[‡] and a very limited number of alkene-inserted complexes have been isolated.[2] The difficulty is probably due to the following reasons. First, alkene-inserted complexes have a low energy pathway of decomposition including β-hydrogen elimination reaction. Secondly, employment of stabilizing ligands such as tertiary phosphines prevents the pre-coordination of alkenes to palladium, making the insertion reaction a high energy process. Recently, Sen succeeded in isolating alkene-inserted complexes by using *trans*-$[Pd(COR)(NCMe)(PPh_3)_2]BF_4$ and *trans*-$Pd(COR)Cl(PPh_3)_2$ (R = Me and Ph) as the starting compounds.[2b,c] In this case, intramolecular chelation through the carbonyl group is considered to stabilise the insertion products. However, this system is applicable only to highly strained alkenes such as norbornene and norbornadiene. We report herein that the cationic acetylpalladium complex having a *cis* geometry *cis*-$[Pd(COMe)(MeCN)(dppe)]BF_4$ **2** [dppe = 1,2-bis(diphenylphosphino)ethane exhibits extremely high reactivity toward simple alkenes to give alkene-inserted complexes.[§]

Acetylpalladium complex **2** prepared *in situ* from *cis*-$[PdMe(MeCN)(dppe)]BF_4$ **1** and CO (1 atm) in CD_2Cl_2 was treated with two equivalents of cyclopentene at −40 °C.[¶] When the reaction was followed by $^{31}P\{^1H\}$ NMR, the signals of complex **2** [δ 40.9 (d) and 29.4 (d), J_{PP} 46 Hz] rapidly disappeared to be replaced by two doublets at δ 54.8 and 33.4 (J_{PP} 32 Hz) assignable to the alkene-inserted complex **3a**, which was isolated as a yellow, crystalline solid after recrystallization from CH_2Cl_2–Et_2O (84% yield). The IR and NMR data indicated that complex **3a** has a five-membered cyclic structure with internal coordination of the carbonyl group as illustrated in Scheme 1.[‖] In the $^{13}C\{^1H\}$ NMR, the signal of α-methyne carbon directly bound to palladium appears as a doublet of doublets at δ 54.8 with large and small couplings with the phosphorus nuclei ($^2J_{PC}$ 83 and 5 Hz). The IR spectrum of **3a** exhibits a strong ν(CO) absorption at 1615 cm^{-1}, the value being in a reasonable region for a carbonyl group coordinating to palladium.[2b]

The alkene-inserted complexes could also be prepared by using cycloheptene (75% yield) and methyl acrylate (74%) instead of cyclopentene. The spectroscopic data showed the cyclic structures similar to **3a**.[‖]

As compared with the reactions described above, reaction of **2** with cyclohexene proceeded rather slowly, and the presence of a large excess of the alkene (100 equiv.) was required for completion of the reaction in CD_2Cl_2 at −40 °C. Furthermore, treatment of **2** with cyclooctene (100 equiv.) under similar reaction conditions gave only a small amount (*ca.* 5%) of the alkene-inserted complex, the formation of which was indicated by the appearance of doublet signals at δ 55.0 and 34.1 (J_{PP} 34 Hz) in the $^{31}P\{^1H\}$ NMR spectrum of the reaction solution.

The difference in reactivity between the cyclic alkenes was examined by competitive experiments. When complex **2** was treated with an equimolar mixture of cyclopentene and cycloheptene (each 10 equiv./2) in CD_2Cl_2 at −40 °C, exclusive formation of **3a** was observed in the $^{31}P\{^1H\}$ NMR spectrum of the reaction solution. Similar experiments were



Scheme 1 *Reagents and conditions*: CO (1 atm), −40 °C, in dichloromethane

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[‡] There are some precedents for the reactions of isolated organopalladium complexes with alkenes to give substituted alkenes which are considered to be formed by alkene-insertion followed by β-hydrogen elimination.[3] These results may be taken as providing indirect evidence for alkene insertion.

[§] A part of the preliminary results has been presented.[4] Very recently, a closely related, independent study on the reactions of cationic *cis*-acetylpalladium complexes with alkenes has been reported in a symposium.[5] The results are consistent with our results.

[¶] The methylpalladium complex **1** was prepared by the reaction of *cis*-$PdMe_2(dppe)$[7] with HBF_4 in acetonitrile and characterised by IR and NMR spectroscopy and elemental analysis. Owing to the instability of the acetyl complex **2** toward decarbonylation to give the methyl complex **1** in the absence of CO, the acetyl complex **2** could not be isolated. The formation of **2** in solution under CO atmosphere has been confirmed by NMR and IR spectroscopy. ^1H NMR (CD_2Cl_2, −40 °C): δ 1.93 (t, *J* 1.5 Hz, 3H, PdCOMe), 2.34 (s, 3H, MeCN), 1.9–2.8 (m, 4H, PCH_2CH_2P), 7.5–7.7 (m, 20H, PPh). $^{31}P\{^1H\}$ NMR (ref. 85% H_3PO_4) (CD_2Cl_2, −40 °C): δ 40.9 (d) and 29.4 (d) (J_{PP} 46 Hz). IR (KBr): 1683 cm^{-1} (CO).

[‖] *Selected spectroscopic data* (^{13}C and ^{31}P NMR and IR) for **3a**–**3c**: NMR signals were performed by using a DEPT pulse sequence.

3a: $^{13}C\{^1H\}$, δ 54.8 (dd, J_{PC} 83 and 5 Hz, Pd*C*H), 64.2 (d, J_{PC} 3 Hz, PdCH*C*H), 240.8 (d, J_{PC} 12 Hz, *C*O), 27.7 (s, *C*H_3), 26.2 (dd, J_{PC} 10 and 5 Hz, *C*H_2 in the cyclopentyl group), 30.5 (d, J_{PC} 5 Hz, *C*H_2 in the cyclopentyl group), 33.6 (d, J_{PC} 4 Hz, *C*H_2 in the cyclopentyl group); $^{31}P\{^1H\}$, δ 54.8 (d) and 33.4 (d) (J_{PP} 32 Hz); IR, 1615 cm^{-1} (CO).

3b: $^{13}C\{^1H\}$, δ 56.2 (dd, J_{PC} 82 and 6 Hz, Pd*C*H), 63.4 (d, J_{PC} 4 Hz, PdCH*C*H), 239.3 (d, J_{PC} 10 Hz, *C*O), 29.2 (s, *C*H_3), 23.9 (s, *C*H_2 in the cycloheptyl group), 30.0 (d, J_{PC} 5 Hz, *C*H_2 in the cycloheptyl group), 30.1 (s, *C*H_2 in the cycloheptyl group), 30.9 (dd, J_{PC} 9 and 5 Hz, *C*H_2 in the cycloheptyl group), 31.3 (d, J_{PC} 9 Hz, *C*H_2 in the cycloheptyl group); $^{31}P\{^1H\}$, δ 56.2 (d) and 33.1 (d) (J_{PP} 33 Hz); IR, 1617 cm^{-1} (CO).

3c: $^{13}C\{^1H\}$, δ 48.8 (d, J_{PC} 76 Hz, Pd*C*H), 50.0 (d, J_{PC} 6 Hz, PdCH*C*H_2), 239.4 (d, J_{PC} 10 Hz, *C*OMe), 29.0 (s, CO*C*H_3), 177.4 (d, J_{PC} 6 Hz, *C*O_2Me), 50.8 (s, CO_2*C*H_3); $^{31}P\{^1H\}$, δ 58.6 (d) and 44.2 (d) (J_{PP} 29 Hz); IR, 1671 and 1620 cm^{-1} (CO).

performed with different pairs of alkenes and the decreasing order of reactivity was determined to be as follows: cycloheptene > cyclohexene > cyclooctene. The highest reactivity of cyclopentene has also been observed in catalytic reactions.[6]

The present results indicate that the insertion of alkene into a palladium–carbon bond is a facile process under appropriate conditions. Complex **2** has a coordination site that is weakly coordinated to acetonitrile and easily accessible to coordination of alkenes. The presence of dppe as a bidentate ligand allows the acetyl group and the coordinated alkene to come to the adjacent sites (*cis*) convenient for the subsequent insertion. Overall insertion of simple alkenes under extremely mild conditions occurs.

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