

COORDINATION-SITE EXCHANGE REACTIONS OF SOME ACETYLACETONATO  
PALLADIUM(II) COMPLEXES: AUTOCATALYSIS AND SELF-CATALYSIS

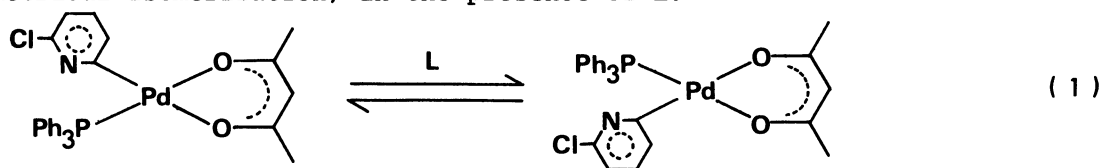
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A novel type of palladium(II) complexes containing a chelated acetylacetonate anion, carbon-bonded pyridyl ligand, and triphenylphosphine were prepared. They undergo the coordination-site exchange catalyzed by the phosphine freed from the reacting complex (autocatalysis) or the nitrogen end of the carbon-bonded pyridine in the reacting species (self-catalysis).

Geometrical isomerizations of square-planar complexes have been the subject of extensive investigation.<sup>1)</sup> Although some complexes such as *cis*-PtCl(aryl)(PPh<sub>3</sub>)<sub>2</sub> isomerize spontaneously in polar solvents,<sup>2)</sup> most of the isomerization reactions proceed in the presence of neutral or anionic free ligands as catalysts,<sup>3)</sup> and two mechanisms, consecutive displacement and polytopal rearrangement of five-coordinate intermediates, are well documented.<sup>1)</sup> The present letter reports on the rapid coordination-site exchange reactions of the Pd(acac)(pyridyl)(PPh<sub>3</sub>) complexes, of which some are catalyzed by PPh<sub>3</sub> freed from the parent complex (autocatalysis) and some by the reacting species itself (self-catalysis).

Preparation of Complexes. The complexes were prepared by the reactions displayed schematically in Fig.1. The novel type of bridging mode of the 2-pyridyl ligand in **2a** was confirmed by X-ray analysis,<sup>4)</sup> and comparative studies on a set of linkage isomers *trans*-PdBr(pyridyl)(PPh<sub>3</sub>)<sub>2</sub> have been reported.<sup>5)</sup> Complex **5f** contains an O-unidentate acac ligand and this bonding mode of  $\beta$ -diketonate anions has been found in some Pt(II)<sup>6,7)</sup> and Pd(II)<sup>8,9)</sup> complexes. All of the newly prepared complexes gave satisfactory analysis and molecular-weight data.

<sup>1</sup>H NMR Studies. As is listed in Table 1, complex **5c** exhibits two methyl signals at 1.70 and 1.92 ppm in conformity with the unsymmetric molecular structure. When a base (L) such as pyridine, 2,6-lutidine, triphenylphosphine, and tri-*o*-tolylphosphine is added to the solution, these signals disappear and instead a broad singlet appears at 1.82 ppm. The other proton signals show no change on addition of the base except appearance of peaks due to L. These results indicate that **5c** is stereochemically rigid in chloroform but undergoes the coordination-site exchange (geometrical isomerization) in the presence of L.



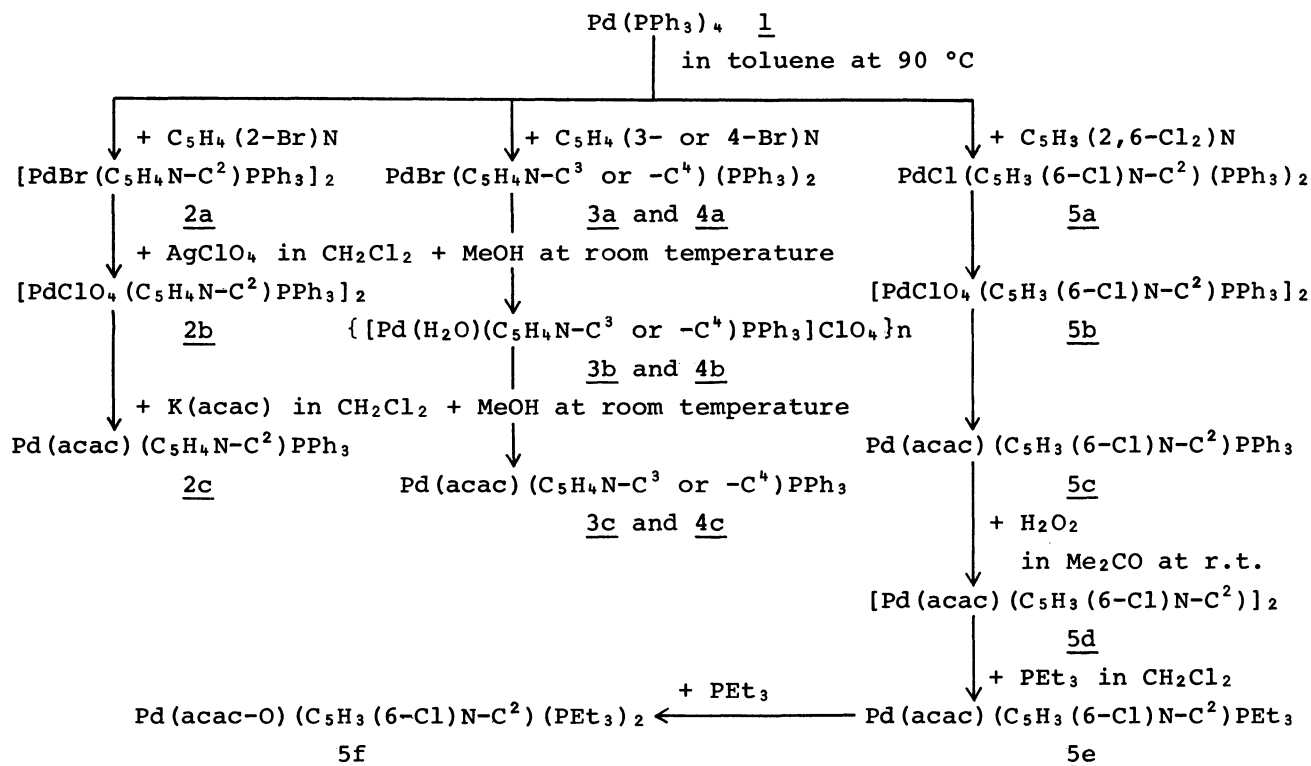


Fig. 1. Schematic representation of the preparative reactions.

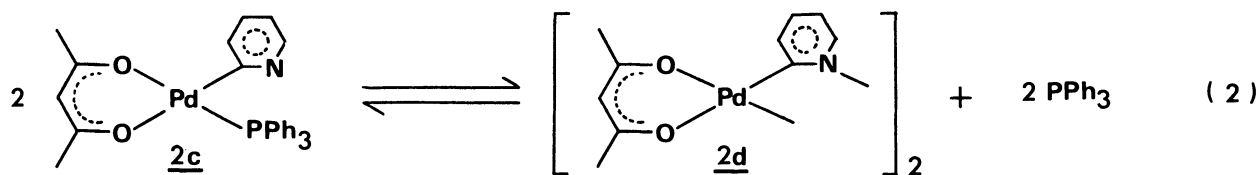
Table 1. Methyl and methine proton signals from the acac ligand  
( $\delta$  in ppm from internal TMS in CDCl<sub>3</sub>)

| No.                     | Complex   | CH <sub>3</sub>  | CH   |
|-------------------------|---|------------------|------|
| <u>2c</u>               | Pd(acac)(C <sub>5</sub> H <sub>4</sub> N-C <sup>2</sup> )PPh <sub>3</sub>                         | 1.82, 2.02, 2.05 | 5.30 |
| <u>2d</u>               | [Pd(acac)(C <sub>5</sub> H <sub>4</sub> N-C <sup>2</sup> )] <sub>2</sub>                          | 2.02, 2.05       | 5.44 |
| <u>3c</u>               | Pd(acac)(C <sub>5</sub> H <sub>4</sub> N-C <sup>3</sup> )PPh <sub>3</sub>                         | 1.82             | 5.41 |
| <u>4c</u>               | Pd(acac)(C <sub>5</sub> H <sub>4</sub> N-C <sup>4</sup> )PPh <sub>3</sub>                         | 1.82             | 5.36 |
| <u>5c</u>               | Pd(acac)(C <sub>5</sub> H <sub>3</sub> (6-Cl)N-C <sup>2</sup> )PPh <sub>3</sub>                   | 1.70, 1.92       | 5.33 |
| <u>5d</u>               | [Pd(acac)(C <sub>5</sub> H <sub>3</sub> (6-Cl)N-C <sup>2</sup> )] <sub>2</sub>                    | 1.94, 2.03       | 5.44 |
| <u>5e</u>               | Pd(acac)(C <sub>5</sub> H <sub>3</sub> (6-Cl)N-C <sup>2</sup> )PEt <sub>3</sub>                   | 1.87, 1.91       | 5.27 |
| <u>5f</u> <sup>a)</sup> | Pd(acac-O)(C <sub>5</sub> H <sub>3</sub> (6-Cl)N-C <sup>2</sup> )(PEt <sub>3</sub> ) <sub>2</sub> | 1.82, 2.11, 2.54 | 5.92 |

a) In 1,2-dichlorobenzene

Various amounts of pyridine was added to a CH<sub>2</sub>Cl<sub>2</sub> solution of 5c (0.1 mol dm<sup>-3</sup>) and the rate of site exchange was determined by the line-shape simulation method at several temperatures below 0 °C. As is seen in Fig.2, the pseudo first order rate constant is proportional to the concentration of pyridine added, and the second order rate constant was obtained as (8.05 ± 0.17) × 10<sup>2</sup>, (2.83 ± 0.08) × 10<sup>2</sup>, (1.03 ± 0.03) × 10<sup>2</sup>, and (2.33 ± 0.29) × 10 dm<sup>3</sup> mol<sup>-1</sup> sec<sup>-1</sup> at 0, -20, -40, and -58 °C, respectively. The Eyring plot of these data gave the activation parameters,  $\Delta H^\ddagger = 25.6 \pm 0.8$  kJ mol<sup>-1</sup> and  $\Delta S^\ddagger = -94.9 \pm 3.0$  J K<sup>-1</sup> mol<sup>-1</sup>. The small  $\Delta H^\ddagger$  and large negative  $\Delta S^\ddagger$  accord with the associative nature of the catalytic reaction.

Complex 2c exhibits three CH<sub>3</sub> resonances (Table 1). Chemical shifts of the two



minor signals exactly coincide with those from 2d, indicating attainment of the equilibrium (Eq.2). Liberated PPh<sub>3</sub> acts as a catalyst for the site exchange of 2c as expressed by (Eq.1), exhibiting a single CH<sub>3</sub> resonance at 1.82 ppm. This effect may be called autocatalysis, since the catalyzing ligand originates from the reacting species. The equilibrium constant of (Eq.2) was determined to be 0.01 mol dm<sup>-3</sup> at 37 °C based on the relative intensities of signals for 2c and 2d. Oxidation of PPh<sub>3</sub> with H<sub>2</sub>O<sub>2</sub> shifts the equilibrium completely to right and the δ 1.82 signal disappears. On the contrary, the <sup>1</sup>H NMR spectrum of 5c shows no sign of coexistence of 5d.

Each of 3c and 4c shows a broad methyl singlet at 1.82 ppm, which becomes broader with decreasing concentration and temperature, and is converted to two broad signals at 1.74 and 1.92 ppm at -60 °C. Thus the singlet at room temperature seems to be caused by the site-exchange catalyzed by a neighboring molecule of the reacting species which is coordinated to the metal atom of the reacting molecule via the nitrogen atom of the pyridyl ligand. This effect may be termed "self-catalysis" since another molecule of the same species acts as a catalyst. The carbon-bonded pyridyl ligand shows higher basicity than free pyridine<sup>5)</sup> and tends to interact with another metal atom, stabilizing the dinuclear structure of 2a and polynuclear structure of 3b and 4b.<sup>10)</sup> Complexes 3c and 4c catalyze Reaction 1 of 5c, too.

As to the mechanism of the coordination-site exchange of the present complexes, the dissociative pathway via a three-coordinate intermediate<sup>2)</sup> is not applicable but the polytopal rearrangement of the five-coordinate intermediate is conceivable, since 5c and 5e do not isomerize in the absence of a Lewis base. (Absence of self-catalysis in these complexes may be related to failure of 2,6-dichloropyridine as a catalyst contrary to 2,6-dimethylpyridine.) By the analogy with the case of M(hfac)<sub>2</sub>PR<sub>3</sub> (M = Pd(II) and Pt(II); hfac = hexafluoroacetylacetonate ion)<sup>11)</sup> and [Pt-CN(phen)<sub>2</sub>]<sub>2</sub>NO<sub>3</sub>,<sup>12)</sup> the following mechanism is proposed which involves the consecutive interchange of the apical and basal coordination sites of a square-pyramid intermediate via a trigonal-bipyramid transition state, where R denotes the pyridyl ligand.

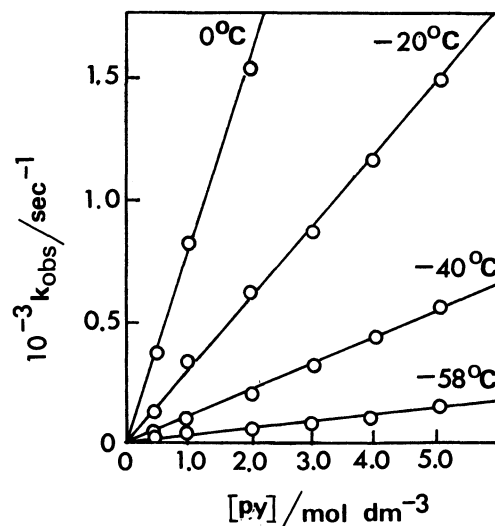
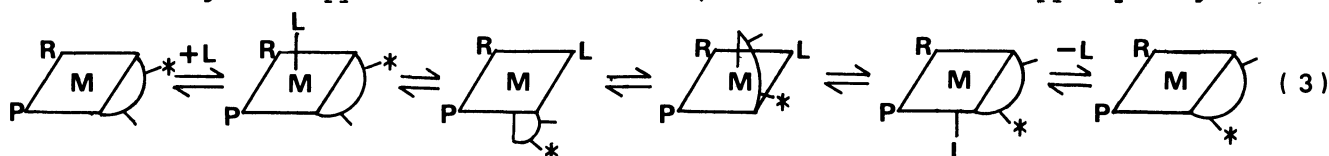
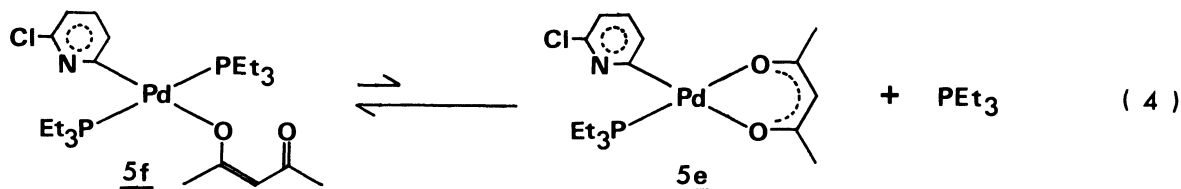
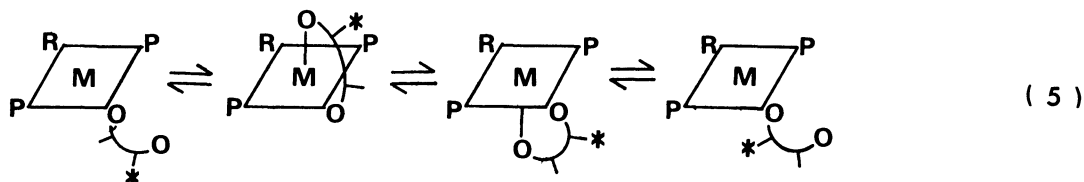


Fig. 2. The pseudo first order rate constant of the coordination-site exchange of 5c in CH<sub>2</sub>Cl<sub>2</sub> as a function of the concentration of added pyridine. Concentration of the complex was kept constant at 0.1 mol dm<sup>-3</sup>.

Complex 5f exhibits three methyl resonances at 1.82, 2.11, and 2.54 ppm in 1,2-dichlorobenzene solution. The minor peak at 1.82 ppm is ascribed to the methyl protons of the chelated acac ligand in 5e which was produced by Eq.4 ( $K = 7.0 \times 10^{-3} \text{ mol dm}^{-3}$ ), and undergoes the site exchange catalyzed by freed  $\text{PEt}_3$ . A little broad signals at 2.11 and 2.54 ppm are assigned to the remote and adjacent methyl protons of the unidentate acac by analogy with data for analogous Pt(II) complexes.<sup>6,7)</sup>



These signals are sharp below 0 °C and become broader at higher temperatures to coalesce at about 70 °C and result in a broad singlet above 80 °C. The signal change with temperature is reversible and the pattern of the  $\text{PEt}_3$  signals remains unchanged. The fluxional motion of the unidentate acac ligand was first observed for  $(\text{CH}_3)_3\text{Si}(\text{acac-O})$ ,<sup>13)</sup> and may be visualized by Eq.5 and seems to offer a helpful support to the proposed mechanism (Eq.3).



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(Received March 30, 1981)