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Organic Syntheses by Means of Noble Metal Compounds. XXXVIII. Cyclohexanone Oxime Complexes of Palladium[1)]

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Ligand exchange reactions of palladium complexes having π-allyl and acetylacetonate as ligands with cyclohexanone oxime were carried out and the formation of several new oxime complexes was reported.

Dioximes as bidentate form stable complexes with various metals, and dimethylglyoxime is a typical example. On the other hand, monoximes do not form a stable complex, and it has been reported that an attempt to prepare a monoxime complex with nickel, iron and cobalt salts gave no stable complex.[2)] Formation of stable monoxime complexes with platinum and palladium[2)] has been reported briefly. We have found that monoximes form stable complexes with palladium by displacing ligands of various palladium complexes. In this paper the ligand exchange reaction of palladium complexes with cyclohexanone oxime is reported.

Results and Discussion

The formation of a stable complex by the reaction of palladium chloride with two moles of cyclohexanone oxime and its structure have already been reported.[3)] The complex can be prepared more easily by treating benzonitrile complex of palladium chloride with the oxime. It was confirmed by X-ray analysis that the complex has a square planar *trans* structure (I). The preparation of the corresponding *cis* complex (II) was attempted

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1) Part XXXVII: T. Susuki and J. Tsuji, This Bulletin, **41**, 1954 (1968).

2) A. V. Babaeva and M. A. Mosyagina, *Dokl. Akad. Nauk S. S. S. R.*, **89**, 293 (1953); *Chem. Abstr.*, **47**, 10392 (1953).

3) M. Tanimura, T. Mizushima and Y. Kinoshita, This Bulletin, **40**, 2777 (1967).

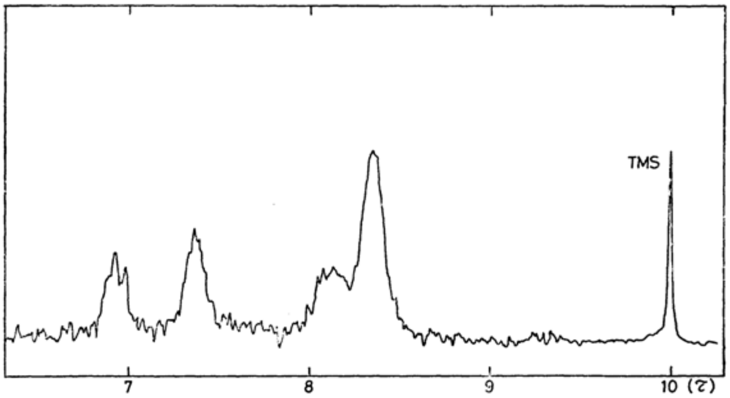
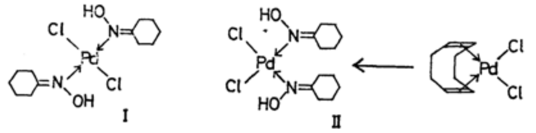


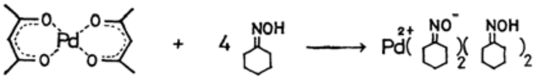
Fig. 1. NMR spectrum of bis(cyclohexanone oxime) palladium chloride (100 Mc/s, in $CDCl_3$).

by the displacement reaction of 1,5-cyclooctadiene-palladium chloride complex with the oxime.

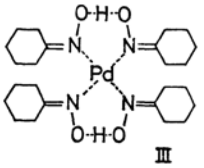


Simple displacement of cyclooctadiene should presumably give the *cis* structure. The complex obtained showed the same IR and NMR spectra as those of the *trans* complex. The only difference was their melting points. The melting point of the *cis* complex, 199°C, was found to be higher than that of the *trans* complex, 184°C. In order to confirm the *cis* structure definitely, the measurement of the dipole moments of both complexes was attempted, but, owing to their low solubilities in benzene, no definite conclusion was obtained. Thus it is not certain whether the complex is really *cis* or not. The NMR spectrum of the *trans* complex is shown in Fig. 1. Two kinds of NMR signals due to the syn and anti α-methylene protons of a cyclohexanone ring are observed at τ 6.91 and τ 7.36. Saito and Nukada[4] reported that, in cyclohexanone oxime hydrochloride, only one kind of α-methylene proton signal is observed, because the paramagnetic anisotropic effect of the hydroxyimino group is eliminated due to the addition of the proton of hydrogen chloride to the lone pair electrons of the nitrogen atom. In the palladium oxime complex, the oxime coordinates to palladium atom with the lone pair electrons of the nitrogen atom, and the separation of the syn and anti proton signals is considered to be attributed to the diamagnetic anisotropic effect of palladium.

From the above mentioned complex formation, it is apparent that cyclohexanone oxime is capable of forming a stable complex with palladium. The oxime complex formation by a ligand exchange reaction of rather stable palladium complexes was attempted. The first example was palladium acetylacetonate, which is a very stable complex. A solution of palladium acetylacetonate in dichloromethane was treated with the oxime at room temperature for 3 min, and a new complex was isolated by the addition of a large amount of ether. The complex showed no IR absorption due to the carbonyl, indicating that the acetylacetone was displaced completely by the oxime. The analysis showed that the complex contained two moles of the oxime anion and two moles of the oxime.



An IR absorption band at 2350 cm^{-1} indicates the presence of hydrogen bonding.[5] The following structure (III) is possible for the complex.



III

π-Allylpalladium chloride was then treated similarly with the oxime in dichloromethane at room temperature. A new complex was isolated by the addition of a large amount of ether. The NMR and IR spectra showed that the complex still retains the π-allyl system and the reaction is not a displacement, but an addition reaction. Analysis showed that one mole of the oxime per two atoms of palladium was incorporated into the complex.

The addition of the oxime molecule by the opening of the bridged structure as shown below (IV) was an expected reaction. The opening of the bridge structure of π-allylpalladium chloride is

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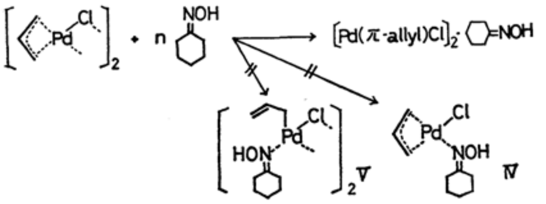
[4] H. Saito, K. Nukada and M. Ohno, *Tetrahedron Letters*, **1964**, 2164.

[5] R. Blinc and D. Hadzi, *J. Chem. Soc.*, **1958**, 4536.

TABLE 1. CHEMICAL SHIFTS AND COUPLING CONSTANTS OF THE π-ALLYL SYSTEM OF $[Pd(\pi\text{-}C_3H_5)Cl]_2C_6H_{10}NOH$ AND $[Pd(\pi\text{-}C_3H_5)Cl]_2$

Complex		τ_1	τ_2	τ_3	J_{12}	J_{13}	Mc/s
$[Pd(\pi\text{-}C_3H_5)Cl]_2C_6H_{10}NOH$	$(CD_3)_2CO$	4.59	5.97	6.96	7.1	11.8	100
	$CDCl_3$	4.56	5.98	6.98	6.8	12.1	60
$[Pd(\pi\text{-}C_3H_5)Cl]_2$6)	$CHCl_3$	4.55	5.98	7.05	7.1	12.1	40

known with such a ligand as phosphine or amine. Another possibility is the opening of the π-allyl system to form σ-allyl bond (V). If these transformations take place, the complex containing one mole of the oxime per one atom of palladium should be obtained. The analysis clearly indicated that these addition reactions did not take place. Even when an excess of the oxime was allowed to react with π-allylpalladium chloride, only one mole of the oxime per mole of the dimeric π-allyl complex was incorporated.



X-Ray crystallographic studies showed that the complex has the structure shown in Fig. 2. Details of the crystallographic studies will be given in a forthcoming paper. In this complex the oxime attaches to one of the palladium atoms by opening the palladium-chlorine bond, forming an unsymmetrical complex. As for the π-allyl system the NMR spectra showed exactly the same pattern as that of the original π-allylpalladium chloride as shown in Table 1. Thus the oxime is quite different from phosphine and other ligands toward π-allyl complex.

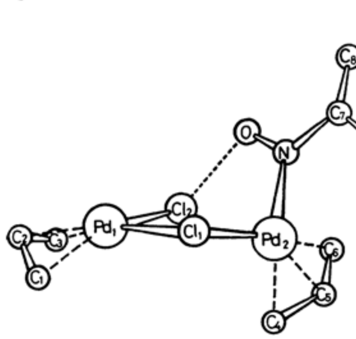
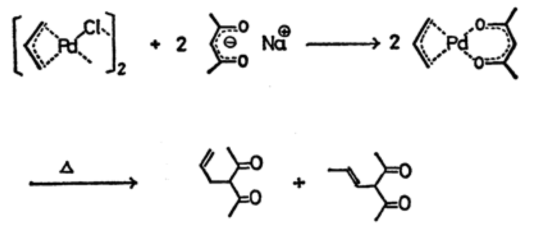


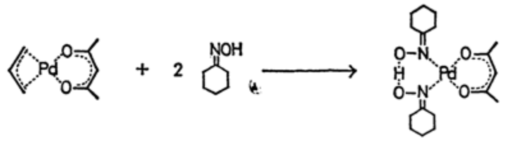
Fig. 2. Schematic drawing of $(Pd(\pi\text{-}C_3H_5)Cl)_2\text{-}C_6H_{10}NOH$.

From the above experiments, it was found that coordinated acetylacetonate is displaced easily with the oxime, and the π-allyl system remained intact when treated with oxime. The reaction of the oxime with π-allylpalladium acetylacetonate was investigated, with the expectation that the acetylacetonate would be displaced. The preparation of π-allylpalladium acetylacetonate was reported by Shaw7) by the reaction of π-allylpalladium chloride with thallium acetylacetonate. We have synthesized the same complex by treating the π-allylpalladium chloride with sodium hydroxide solution of acetylacetone.



The complex is not stable and decomposes slowly on standing. When heated at 90°C under reduced pressure, the complex decomposed to give 3-allyl-2,4-pentanedione, accompanied by 3-propenyl-2,4-pentanedione. The products were formed by the coupling of the two ligands coordinated to the palladium. A somewhat stable complex was obtained by the reaction of π-(1-ethoxycarbonylmethyl-3-ethoxycarbonylallyl)palladium chloride with sodium acetylacetonate in benzene.

The reaction of the oxime with π-allylpalladium acetylacetonate in ether proceeded somewhat violently and yellow crystals separated. Infrared spectrum showed the presence of the acetylacetonate system in the new complex. Thus it is apparent that unexpectedly the π-allyl system was displaced with the oxime instead of the acetylacetonate system.



VI

An IR band at 2350 cm^{-1} indicates the presence of hydrogen bonding and the structure (VI) is proposed for the complex.

From the results described in this paper, it is

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6) B. L. Shaw and N. Sheppard, *Chem. Ind. (London)*, **1961**, 517.

7) S. D. Robinson and B. L. Shaw, *J. Chem. Soc.*, **1963**, 4806.

apparent that the oxime coordinates to palladium to form stable complexes. Stable ligands such as π-allyl or acetylacetonate can be displaced with the oxime quite easily.

Experimental

Reaction of π-Allylpalladium Chloride with Cyclohexanone Oxime. Bis(π-allyl)palladium chloride (1.83 g) was dissolved in a minimum amount of dichloromethane, and cyclohexanone oxime (0.57 g) was added. The mixture was stirred for 3 min until a complete solution was obtained. Then, a large amount of ether was added to ensure the precipitation to give 2.13 g of a pale yellow complex. The complex was washed well with ether and then recrystallized from a mixture of dichloromethane and ether. On standing in air the complex decomposes slowly. When heated it darkens at 121—131°C and decomposes at 134°C.

Found: C, 30.27; H, 4.56; N, 2.80; Cl, 15.10%. Calcd for $C_{12}H_{21}NOPd_2Cl_2$: C, 30.09; H, 4.42; N, 2.92; Cl, 14.80%.

Reaction of palladium acetylacetonate with cyclohexanone oxime.

Reaction of Palladium Acetylacetonate with Cyclohexanone Oxime. Palladium acetylacetonate (1 g) and cyclohexanone oxime (2 g) were mixed in dichloromethane and the mixture was shaken for 3 min. Pale yellow crystals were obtained by the addition of a large amount of ether. The complex was recrystallized twice from ether-dichloromethane mixture. Mp 167°C. Found: C, 51.65; H, 7.68; N, 9.96%. Calcd for $C_{24}H_{42}N_4O_4Pd$: C, 51.75; H, 7.60; N, 10.05%.

Preparation of π-Allylpalladium Acetylacetonate. Acetylacetone (1 g) and sodium hydroxide (0.4 g) were dissolved in 10 m*l* of water and the solution was poured into a separatory funnel. Then π-allylpalladium chloride (1.83 g) and 30 m*l* of ether were added to the funnel, and the mixture was shaken for 3 min, when the complex dissolved completely. The ethereal layer was separated and the ether was evaporated. From the residue, pale yellow crystals were obtained, which were washed with water. The crystals were purified by subliming twice at 50—60°C/2 mmHg to give colorless crystals; mp 72—73°C. The complex decomposes on standing at room temperature. Found: C, 39.00; H, 4.97%; mol wt, 243. Calcd for $C_8H_{12}O_2Pd$; C, 38.97; H, 4.91%; mol wt, 246.5.

Decomposition of π-Allylpalladium Acetylacetonate. The complex (4.8 g) was heated in an oil bath at 100°C under reduced pressure (30 mmHg), and a liquid (1.2 g) was obtained at 83—90°C/30 mmHg. The liquid was purified by preparative gas chromatography to give 3-allyl-2,4-pentanedione. The structure was determined by NMR and IR spectra. Found; C, 68.71; H, 8.86%; mol wt, 139. Calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.63%; mol wt, 140.18.

Preparation of π-(1-Ethoxycarbonylmethyl-3-ethoxycarbonylallyl)palladium Acetylacetonate. 1-Ethoxycarbonylmethyl-3-ethoxycarbonylallyl palladium chloride (2.55 g) and sodium acetylacetonate (0.92 g) were mixed in 20 m*l* of benzene and the mixture was stirred at room temperature for 30 min. After the reaction, benzene was removed at 2 mmHg and the residue was extracted with ether. By evaporating the ether, pale yellow crystals were obtained, which are more stable than π-allylpalladium acetylacetonate, but decomposes slowly on standing. Found: C, 44.74; H, 5.49%. Calcd for $C_{15}H_{22}O_6Pd$: C, 44.51; H, 5.48%.

Reaction of π-allylpalladium acetylacetonate with cyclohexanone oxime.

Reaction of π-Allylpalladium Acetylacetonate with Cyclohexanone Oxime. π-Allylpalladium acetylacetonate (2.46 g) was dissolved in 25 ml of ether, and the oxime (2.16 g) in 15 m*l* of ether was added. The mixture was shaken for 3 min. When it was warmed on a steam bath, a violent reaction was observed and yellow crystals appeared to give 2.9 g of a crude product which was recrystallized from dichloromethane and ether twice to give crystals, mp 149—150°C. Found: C, 47.45; H, 6.57; N, 6.66%. Calcd for $C_{17}H_{18}N_2O_4Pd$; C, 47.40; H, 6.55; N, 6.50%.

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