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Aromatic Metalation Reactions by Palladium(II) and Platinum(II) on Aromatic Aldoximes and Ketoximes

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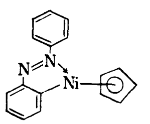
Ortho metalation by palladium(II) was observed in the reaction of lithium tetrachloropalladate(II) with various aromatic aldoximes and ketoximes in methanol in the presence of sodium acetate. The obtained chloro-bridged complexes(**7**) possessed both *ortho*-attached palladium-carbon σ-bonding and palladium-nitrogen coordinate bonding to oximes. Reactions of *O*-acyl and *O*-methyl oximes with lithium tetrachloropalladate(II) were also carried out. An *ortho* metalation was observed in the former case, but dichlorobis(*O*-methyl oxime)palladium(II) type complexes containing no palladium-carbon σ-bonds were predominantly formed in the latter case. The bridge-splitting reaction of chloro-bridged complexes with triphenylphosphine and the metathetic reaction with sodium bromide in acetone were carried out. In the case of potassium tetrachloroplatinate(II), an *ortho* metalation reaction was observed giving the complexes(**10**) but chloro-bridged complexes could not be isolated.

It has recently been shown that direct electrophilic aromatic substitution reactions by nickel(II), palladium(II), and platinum(II) on azobenzene,[1,2] *N*,*N*-dimethylbenzylamine,[3] 2-phenylpyridine,[4] and benzylidenaniline[5] gave the following complexes (**1**—**5**), respectively.



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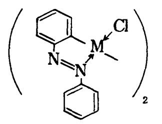

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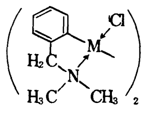

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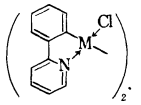

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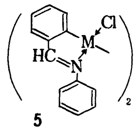

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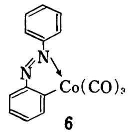

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M=Pd, Pt

Transition metal complexes containing carbon-metal σ-bonds are usually very unstable[6] but the above complexes are surprisingly stable against air and heat. On the other hand, palladium-aromatic ring σ-bonded complexes may be regarded as intermediates in the reactions,[7-11] although they are unstable and not isolated.

Heck[12] prepared complex **6** and considered it to be the reaction intermediate of the carbonylation of azobenzene catalyzed by dicobalt octacarbonyl; this reaction was first discovered by Horiie and Murahashi.[13] Tsuji *et al.* obtained 2-(dimethylaminomethyl)stilbene by the reaction of complex **3** with styrene in acetic acid.[14]

From the above arguments, transition metal-aromatic ring σ-bonded complexes are important for studying the mechanism of aromatic substitution reactions and the study of the properties of these complexes will help to find out new synthetic methods.

Here we report a new metalation reaction by palladium(II) and platinum(II) on aromatic aldoximes and ketoximes.[15]

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[1] J. P. Kleiman and M. Dubeck, *J. Amer. Chem. Soc.*, **85**, 1544 (1963).

[2] A. C. Cope and R. W. Siekman, *ibid.*, **87**, 3272 (1965).

[3] A. C. Cope and E. C. Friedrich, *ibid.*, **90**, 909 (1968).

[4] A. Kasahara, This Bulletin, **41**, 1272 (1968).

[5] S. P. Molnar and M. Orchin, *J. Organometal. Chem.*, **16**, 196 (1969).

[6] G. E. Coates, M. L. H. Green and K. Wade, "Organometallic Compounds," Vol. 2, Methuen & Co., Ltd., London (1968), p. 203.

[7] R. van Helden and C. Verberg, *Rec. Trav. Chim. Pays-Bas*, **84**, 1263 (1965).

[8] I. Moritani and Y. Fujiwara, *Tetrahedron Lett.*, **1967**, 1119.

[9] Y. Fujiwara, I. Moritani, S. Danno, R. Asano and S. Teranishi, *J. Amer. Chem. Soc.*, **91**, 7166 (1969).

[10] T. Sakakibara, S. Nishimura, Y. Odaira and T. Yoshida, *Tetrahedron Lett.*, **1969**, 1061.

[11] R. F. Heck, *J. Amer. Chem. Soc.*, **90**, 5518, 5526, 5531, 5535, 5538, 5542 (1968).

[12] R. F. Heck, *ibid.*, **90**, 313 (1968).

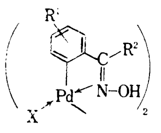
[13] S. Horiie and S. Murahashi, This Bulletin, **33**, 88 (1960).

[14] H. Takahashi, K. Ohno and J. Tsuji, Abstract III, the 22nd Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1969, p. 1595.

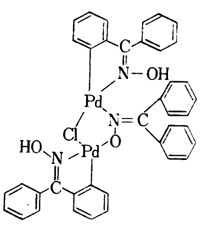
Results and Discussion

It was found that benzophenone oxime gave 3-phenylphthalimidine by carbonylation in the presence of dicobalt octacarbonyl[19] or palladium chloride[20] in benzene. We studied the reaction benzophenone oxime with palladium chloride in the absence of carbon monoxide.

The reaction of benzophenone oxime with lithium tetrachloropalladate(II) in methanol at room temperature gave dichlorobis(benzophenone oxime) palladium(II) having no palladium-carbon σ-bondings. When the reaction was carried out by adding sodium acetate, we obtained complex **7a** (R^1=H, R^2=C_6H_5, X=Cl) and a small amount of complex **8**. The structure of **7** will be discussed in detail later. Complex **8** was tentatively assigned as follows by analysis and molecular weight determination. This complex seems to be obtained from **7a** and benzophenone oxime by eliminating hydrogen chloride. A similar reaction of opening the palladium-chlorine bond in π-allylic palladium(II) chloride with cyclohexanone oxime was reported by Imamura *et al.*[17]



7a—j



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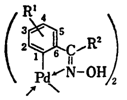
The procedure of adding sodium acetate as an acceptor of hydrogen chloride formed by the reaction was successfully applied to various aromatic aldoximes and ketoximes. The resulting complexes analogous to **7a** are shown in Table 1. The corresponding bromo-bridged complexes were obtained by the metathetic reaction of the chloro-complexes with sodium bromide in acetone. All the complexes were stable against air and heat, and complexes except for those from benzophenone, *n*- and isobutyrophenone oxime were insoluble in the usual organic solvents. The reaction product was deposited from the reaction mixture, but in some cases it was necessary to add water to isolate a complex. In the case of acetophenone oxime and its derivatives, their complexes were also obtained in the absence of sodium acetate but the yields were lower and the rate of the reaction slower judging from the disappearing rate of the black-red color of lithium tetrachloropalladate(II). Although *syn*- and *anti*-isomers exist in general in oximes, we used stable *syn*-aldoximes

TABLE 1. AROMATIC METALATION BY PALLADIUM (II) ON VARIOUS AROMATIC OXIMES



Compound	R^1	R^2	X	Yield (%)	Mp (°C)	ν_{O-H} (cm^{-1})*1	$\nu_{C=N}$ (cm^{-1})*1
7a	H	C_6H_5	Cl	67.8	150—152	3343	1625
7a'	H	C_6H_5	Br	91	190—197(d)*2	3345	1621
7b	H	CH_3	Cl	95.1(53.1)*3	210—(d)	3426	1640
7b'	H	CH_3	Br	88	259—260(d)	3423	1638
7c	3-CH_3O	CH_3	Cl	91.3	245—250(d)	3460, 3433	1629
7d	3-NO_2	CH_3	Cl	79.3	>270	3447	1630
7e	H	$CH_2CH_2CH_3$	Cl	92.8	188—205(d)	3425	1625
7f	H	$CH(CH_3)_2$	Cl	84.2	189—191(d)	3370	1627
7g	3,4-Benzo	CH_3	Cl	98.3	>270	3420	1617
7h	4,5-Benzo	CH_3	Cl	32.5	238—239(d)	3370	1615
7i	H	H	Cl	77.1	200—(d)	3410	1622
7j	3-CH_3O	H	Cl	56.8	195—197(d)	3415	1628

*1 Measured in Nujol mulls or KBr disks.
*2 d: decomposition.
*3 Reaction was carried out in the absence of sodium acetate for 20 hr at room temperature.

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15) It has been reported in several papers that monoximes form stable dichlorobis(oxime)palladium(II) type complexes having no palladium-carbon σ-bonds.[16-18]

16) A. V. Babaeva and M. A. Mosyagina, *Dokl. Akad. Nauk SSSR*, **89**, 293 (1953); *Chem. Anst.*, **47**, 10392 (1953).

17) S. Imamura, T. Kajimoto, Y. Kitano and J. Tsuji, This Bulletin, **42**, 895 (1969).

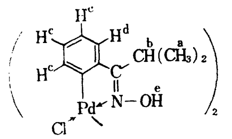
18) T. Takiguchi, K. Kurosaki and M. Abe, *Kogyo Kagaku Zasshi*, **72**, 1549 (1969).

19) A. Rosenthal, R. F. Astbury and A. Hubscher, *J. Org. Chem.*, **33**, 1037 (1958).

20) H. Onoue, unpublished result.

and *anti*-phenylalkyl ketoximes. In the case of isobutyrophenone oxime, both isomers were stable and the isolated isomers were tested for the reaction. As suggested by the structure of the complexes, and *anti*-isomer gave an expected complex (**7f**) in good yield, but the *syn*-isomer gave a different complex, which was not studied further.

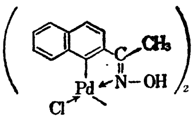
The structure of the complexes was established by the following data. The molecular weights of complexes **7a**, **7e** and **7f** in chloroform coincided well with the values calculated for the chloro-bridged dimers. The IR spectra showed the characteristic O–H stretching frequency in the 3310—3460 cm^{-1} region and the C=N stretching frequency in the 1615—1640 cm^{-1} region as shown in Table 1. On the other hand, the C=N stretching frequency in conjugated oximes in solution is known to fall in the range 1630—1660 cm^{-1}, with slightly lower values for solides.[21] It was concluded therefore that the coordination of oximes to palladium in the complexes was established through the lone pair of nitrogen but not through the C=N π-system.[5,22] The NMR spectrum of complex **7f** was in good agreement with the proposed structure, showing a doublet at 1.38 (J=7 Hz, 6H), a septet at 3.35 (J=7 Hz, 1H), two multiplets at 6.76—7.13 (3H) and 7.23—7.46 (1H) and a singlet at 8.20 ppm (1H), each corresponding to a, b, c, d and e, respectively. This result shows that one aromatic ring proton *ortho* to the C=N group was substituted by palladium(II).



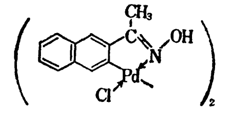
7f

Lithium aluminum deuteride reduction[23] of the acetophenone oxime-palladium(II) chloride complex gave deuterated *dl*-α-phenylethylamine.[24] Its NMR spectrum showed that the incorporation of deuterium had occurred in the phenyl ring and the methine group, a triplet at 1.32 ppm corresponding to methyl protons (J=1 Hz, 3H) and a singlet at 7.25 ppm corresponding so phenyl protons (4H). After treatment with water to exchange deuterium of the amino group with proton, its acetyl derivative was prepared. It was determined by mass spectrometry that the acetyl derivative contained 2% of d_0, 18% of d_1 and 80% of d_2 species.

Although the *ortho* metalation by palladium(II) was confirmed, there are two positions in 2-acetonaphthon oxime, 1 and 3, susceptible to metalation by palladium(II), giving the following complexes, **A** and **B**, respectively.



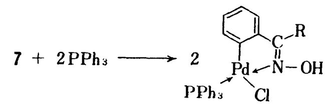
A



B

The obtained complex was reduced with lithium aluminum deuteride to give deuterated 2-(α-aminoethyl)naphthalene. From the ratio of α- to β-protons on the naphthalene ring calculated from its NMR spectrum, it was established that **B** was the correct one. The structure of the 1-acetonaphthon oxime complex (**7h**) was confirmed by the same method.

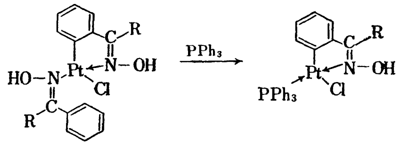
The chloro-bridged complexes (**7**) reacted with triphenylphosphine to give the corresponding bridge-splitted complexes (**9**). In contrast to the other complexes, complex **7i** reacted with a theoretical amount of triphenylphosphine to give complex **9c**,



9a: R=C_6H_5
9b: R=CH_3
9c: R=H

but with an excess of triphenylphosphine to give a new complex containing two moles of triphenylphosphine per palladium.

The metalation reaction by palladium(II) was extended to the reaction of oximes with platinum(II). However, the reaction of one-molar quantity of acetophenone oxime and sodium acetate with potassium tetrachloroplatinate(II) in aqueous methanol gave only an intractable black material which deposited platinum metal on dissolving in dichloromethane. When the reaction was carried out in the absence of sodium acetate, complex **10a** was obtained. The IR spectrum was the same as that of the palladium analogue which was prepared from complex **7b** by a bridge-splitting reaction with acetophenone oxime. Complex **10a** reacted with triphenylphosphine giving complex **11**. *anti*-Isobutyrophenone oxime gave also complex **10b**.



10a: R=CH_3
10b: R=$CH(CH_3)_2$

11: R=CH_3

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[21] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley & Sons, New York, (1957), p. 270.

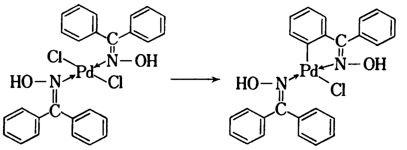
[22] M. Orchin and P. J. Schmidt, *Coord. Chem. Rev.*, **2**, 345 (1968).

[23] Metal hydride reduction of carbon-metal σ-bonds was often tried. See Ref. 3 and the references cited.

[24] Reduction of oxime to amine is a well-known reaction.

Thus the electrophilic attack by platinum(II) on the aromatic ring of oximes could occur but the chloro-bridged complexes could not be obtained. It is probable that the differences observed in the case of palladium(II) and platinum(II) are partly attributed to the poor reactivity of platinum(II) compared to palladium(II).

These reactions by palladium(II) and platinum(II) on aromatic oximes would probably proceed through an initial coordination of nitrogen to the metal followed by an electrophilic substitution by the metal at an *ortho* position on the aromatic ring. In fact, the following metalation reaction occurred in boiling tetrahydrofuran yielding complex **12**.



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Thus it can be expected that if nitrogen coordinates strongly to the metal, dichlorobis(oxime)-metal type complexes are formed and no metalation reaction can take place. We studied the reaction of *O*-methyl and *O*-acyl derivatives with lithium tetrachloropalladate(II).

O-Methyl oxime of benzophenone and acetophenone yielded predominantly dichlorobis(*O*-methyl oxime)palladium(II) even in the presence of sodium acetate. It may be concluded that the strong coordination to palladium with nitrogen due to the presence of the electron donating methyl group reduced the formal charge of palladium(II), preventing its electrophilic attack on the aromatic ring.

On the other hand, *O*-acetyl and *O*-benzoyl acetophenone oxime, in which the coordinating power of nitrogen would be reduced by the presence of electron withdrawing acyl groups, gave complex **7b** in the absence of sodium acetate. In addition, methyl benzoate was isolated in the reaction of *O*-benzoyl acetophenone oxime. It is uncertain whether the methanolysis of *O*-acyl groups occurred before or after the formation of a palladium-carbon σ-bond.

Experimental

Melting points were determined on a Yanagimoto micro-stage apparatus and uncorrected. IR spectra were recorded with Nippon Bunko IR-S and Nippon Bunko Model DS-402G Spectrometers. NMR spectra were determined at 60MHz with a Varian A-60 Spectrometer in deuteriochloroform using tetramethylsilane as an internal standard. Molecular weights were determined with a Mechrolab Model 301A vapor pressure osmometer in a chloroform solution.

Materials. Anhydrous palladium chloride was obtained from Nippon Engelhard, Ltd. Potassium tetrachloroplatinate(II) was obtained from Wako Pure Chemicals Industries, Ltd. Lithium aluminum deuteride was obtained from Metal Hydrides, Inc. A lithium tetrachloropalladate(II) solution in methanol (0.5 M) was prepared by stirring two equivalents of anhydrous lithium chloride and one equivalent of anhydrous palladium chloride in methanol until a homogeneous solution was formed. Each oxime was prepared from the corresponding aldehyde or ketone, hydroxylamine hydrochloride and sodium hydroxide in the usual manner and purified by recrystallization or distillation before use. *Syn*- and *anti*-isobutyrophenone oximes were separated from the mixture by fractional crystallization from *n*-hexane.[25]

Reaction of Benzophenone Oxime with Lithium Tetrachloropalladate(II). When a solution containing 3.95 g (0.02 mol) of benzophenone oxime and 0.01 mol of Li_2PdCl_4 in 40 m*l* of methanol was allowed to stand for 5 days at room temperature, 2.86 g of red-yellow crystals, mp 180°C dec., was obtained. IR spectrum (Nujol): 3280 and 3200 cm^{-1} (ν_{O-H}); 1629 cm^{-1} ($\nu_{C=N}$).

Found: C, 54.45; H, 4.03; N, 5.05; Pd, 18.53%. Calcd for $C_{26}H_{22}N_2O_2PdCl_2$: C, 54.61; H, 3.89; N, 4.90; Pd, 18.61%.

A solution of 2.00 g of the complex in 30 m*l* of tetrahydrofuran was boiled for 1 hr and cooled to give 0.84 g of the starting complex. Upon addition of *n*-hexane to the filtrate, 0.13 g of the complex was further recovered. Pale yellow solids were then formed from this filtrate by a further addition of *n*-hexane followed by standing for 2 days. Solids were recrystallized from chloroform-*n*-hexane to give 0.71 g of complex **12**, mp 192—200°C. IR spectrum (Nujol): 3245 sh, 3160 and 3105 cm^{-1} (ν_{O-H}); 1619 cm^{-1} (broad, $\nu_{C=N}$).

Found: C, 58.04; H, 4.18; Cl, 6.81%. Calcd for $C_{26}H_{21}N_2O_2PdCl$: C, 58.33; H, 3.96; Cl, 6.62%. The complex was also prepared from complex **7a** by a bridge-splitting reaction with benzophenone oxime.

Preparation of Halogen-Bridged Complexes. All complexes were prepared as yellow or orange-yellow solids by the following general procedures. Complexes **7a**, **7a′**, **7e** and **7f** were soluble in dichloromethane, chloroform, acetone and tetrahydrofuran, but other complexes were insoluble in ordinary organic solvents. The yields and physical properties and analytical data are summarized in Tables 1 and 2.

(a) Complexes **7a**, **7d**, **7f**, **7h**, **7i** and **7j**. To a solution containing 0.02 mol of Li_2PdCl_4 in 40 m*l* of methanol, a methanol solution of 0.02 mol of oxime and 0.02 mol of oxime and 0.02 mol of sodium acetate trihydrate was added. When the solution was allowed to stand for one or two days at room temperature, small amounts of precipitates were formed and the black-red colour of the solution turned pale yellow. The mixture was filtered and water was added to the filtrate to give yellow solids. Other oximes except for benzophenone, anisaldehyde, and 1-acetonaphthon oxime gave analytically pure complexes **7d**, **7f** and **7i**.

Yellow solids obtained in the case of benzophenone

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[25] H. M. Kissman and J. Williams, *J. Amer. Chem. Soc.*, **72**, 5323 (1950).

TABLE 2. ANALYTICAL DATA FOR COMPLEXES **7a**—**j**

Compound	Formula	Analyses found (Calcd.) (%)				
		C	H	N	Cl	Pd
7a[*1]	$C_{26}H_{20}N_2O_2Pd_2Cl_2$	46.26 (46.18)	3.13 (2.99)	3.87 (4.14)		
7a′	$C_{26}H_{20}N_2O_2Pd_2Br_2$	41.12 (40.81)	2.76 (2.64)			27.86 (27.81)
7b	$C_{16}H_{16}N_2O_2Pd_2Cl_2$	34.85 (34.81)	2.97 (2.93)	4.88 (5.08)	12.39 (12.84)	
7b′	$C_{16}H_{16}N_2O_2Pd_2Br_2$	30.33 (29.98)	2.62 (2.52)			
7c	$C_{18}H_{20}N_2O_4Pd_2Cl_2$	35.41 (35.32)	3.33 (3.30)	4.43 (4.58)	11.29 (11.58)	
7d	$C_{16}H_{14}N_4O_6Pd_2Cl_2$	30.05 (29.93)	2.31 (2.20)	8.43 (8.73)	11.26 (11.04)	
7e[*2]	$C_{20}H_{24}N_2O_2Pd_2Cl_2$	39.99 (39.50)	3.99 (3.99)	4.58 (4.61)		35.01 (34.99)
7f[*3]	$C_{20}H_{24}N_2O_2Pd_2Cl_2$	39.70 (39.50)	4.02 (3.99)			
7g	$C_{24}H_{20}N_2O_2Pd_2Cl_2$	44.25 (44.20)	3.26 (3.10)	4.17 (4.30)		32.25 (32.63)
7h	$C_{24}H_{20}N_2O_2Pd_2Cl_2$	43.85 (44.20)	3.14 (3.10)	3.96 (4.30)		32.43 (32.63)
7i	$C_{14}H_{12}N_2O_2Pd_2Cl_2$	32.68 (32.08)	2.34 (2.34)			39.93 (40.61)
7j	$C_{16}H_{16}N_2O_2Pd_2Cl_2$	32.96 (32.90)	3.01 (2.77)			35.45 (36.44)

[*1] mol wt, 732 (676.18). [*2] mol wt, 622 (608.16). [*3] mol wt, 597 (608.16).

oxime were separated into two complexes **7a** and **8** by fractional crystallization from dichloromethane-*n*-hexane. Complex **8** was obtained as pale yellow crystals, 0.97 g, mp 200—216°C dec.

Found: C, 56.39; H, 3.78; N, 4.99; Cl, 4.82%; mol wt, 806. Calcd for $C_{39}H_{30}N_3O_3Pd_2Cl$: C, 55.96; H, 3.62; N, 5.02; Cl, 4.24%; mol wt, 836.97.

Yellow solids from anisaldexime were dissolved in dichloromethane. When the solution was concentrated, complex **7j** was obtained which, once isolated, was insoluble in most organic solvents.

Treatment of yellow solids from 1-acetonaphthon oxime with boiling chloroform left pure complex **7h**.

(b) Complexes **7b**, **7c**, **7e** and **7g**. Reactions were carried out according to the same procedure as above, but in these cases the expected complexes precipitated from the solution. The reaction mixtures were then filtered, washed with methanol and water and dried to give pure complexes.

(c) Complexes **7a′** and **7b′**. Complex **7a** or **7b** reacted with sodium bromide in aqueous acetone for an hour at room temperature or by refluxing on a water bath. The yellow solution was concentrated and water was added to give yellow solids.

Preparation of Complexes (9). To a suspension of complex **7a** (0.10 g) in dichloromethane (0.5 m*l*) was added triphenylphosphine (0.10 g). The resulting solution was diluted with *n*-hexane, whereupon complex **9a** was obtained as pale yellow crystals (0.159 g, 89%), mp 203—210°C dec. Purification was accompanied by recrystallization from dichloromethane-*n*-hexane. IR spectrum (Nujol): 3180 cm^{-1} (ν_{O-H}).

Found: C, 62.00; H, 4.26; Cl, 6.07%; mol wt, 558. Calcd for $C_{31}H_{25}NOPPdCl$: C, 62.01; H, 4.21; Cl, 5.90%; mol wt, 600.39.

Similarly complex **9b** was prepared from complex **7b** as yellow crystals, mp 205—211°C dec. IR spectrum (Nujol): 3195 cm^{-1} (ν_{O-H}); 1266 cm^{-1} (CH_2Cl_2). Found: C, 53.39; H, 4.20%. Calcd for $C_{26}H_{23}NOPPdCl \cdot 3/4CH_2Cl_2$: C, 53.37; H, 3.88%.

Complex **9c** was similarly prepared from complex **7i**, as orange crystals, mp 173—174°C dec. IR spectrum (Nujol): 3220 cm^{-1} (ν_{O-H}).

Found: C, 56.88; H, 4.34%. Calcd for $C_{25}H_{21}NOPPdCl$: C, 57.27; H, 4.04%.

Reaction of Complex (7i) with an Excess of Triphenylphosphine. A suspension of 0.262 g (0.5 mmol) of complex **7i** in 1 m*l* of chloroform turned to a yellow solution on adding 0.577 g (2.2 mmol) of triphenylphosphine. Addition of *n*-hexane to the solution gave 0.720 g (93%) of pale yellow crystals, melting at 188—192°C and then solidifying, followed by decomposition at 196—197°C. The complex was found to be completely dissociated in solution from its IR spectrum in chloroform and the molecular weight. IR spectrum (ν_{O-H}): 3390 cm^{-1} (in Nujol); 3220 cm^{-1} (chloroform).

Found: C, 65.03; H, 4.59%; mol wt, 395. Calcd for $C_{43}H_{36}NOP_2PdCl$: C, 65.05; H, 4.62%; mol wt, 786.59.

Reduction of Complexes (7) with Lithium Aluminum Deuteride. To a mixture of 1.00 g of the complex to be reduced in 20 m*l* of absolute tetrahydrofuran was added 0.50 g of lithium aluminum deuteride with stirring. After stirring for 30 min at room temperature, the resulting black mixture was worked up by careful addition of 2 m*l* of deuterium oxide followed by the addition of anhydrous sodium sulfate. The mixture was filtered and washed well with tetrahydrofuran. Removal of tetrahydrofuran gave crude amine. This was purified by distillation or by transformation to its hydrochloride or acetyl derivative.

Reaction of Oxime with Potassium Tetrachloroplatinate (II). A solution of 2.41 mmol of oxime in 10 m*l* of methanol was added to a solution of 2.41 mmol of K_2PtCl_4 in 20 m*l* of water. The initially clear red solution became lighter in colour and dark yellow solids precipitated. After standing for 2 days, the solids were filtered and purified by passing a short silica gel column with dichloromethane followed by recrystallization from dichloromethane-*n*-hexane.

Complex **10a** was obtained from acetophenone oxime, as yellow crystals (0.158 g), mp 190—193°C. IR spectrum (Nujol): 3310 and 3230 cm^{-1} (ν_{O-H}); 1644 and 1633 cm^{-1} ($\nu_{C=N}$).

Found: C, 38.48; H, 3.53; Pt, 38.69%. Calcd for $C_{16}H_{17}N_2O_2PtCl$: C, 38.44; H, 3.43; Pt, 39.03%.

Complex **10b** was obtained from *anti*-isobutyrophenone oxime, as yellow crystals (0.045 g), mp 178—180°C. IR spectrum (Nujol): 3360 and 3230 cm^{-1} (ν_{O-H}); 1630 sh and 1623 cm^{-1} ($\nu_{C=N}$).

Found: C, 43.11; H, 4.59; Pt, 34.57%. Calcd for $C_{20}H_{25}N_2O_2PtCl$: C, 43.20; H, 4.54; Pt, 35.09%.

A solution of complex **10a** (0.050 g) in 0.5 m*l* of dichloromethane was treated with triphenylphosphine (0.050 g) and *n*-hexane was added, whereupon complex **11** (0.058 g, 92%) was obtained as yellow crystals, mp 254—256°C. Its IR spectrum was consistent with that of the palladium analogue (**9b**) and showed a band at 1266 cm^{-1} due to dichloromethane. Found: C, 47.40; H, 3.82; Cl, 10.60%. Calcd for $C_{26}H_{23}NOPPtCl\cdot 1/2CH_2Cl_2$- C, 47.55; H, 3.62; Cl, 10.59%.

Reaction of *O*-Methyl Benzophenone Oxime with Lithium Tetrachloropalladate (II). Reaction was carried out in the same manner as the preparation of complex **7a** using 0.01 mol of *O*-methyl benzophenone oxime and other reactants. After standing for 16 hr, the resulting yellow solids were filtered. More solids were obtained from the filtrate by extracting with chloroform. The solids were separated into two kinds of compounds by fractional crystallization from chloroform-*n*-hexane. Dichlorobis(*O*-methyl benzophenone oxime)palladium(II), the more soluble compound in chloroform, was obtained as yellow-brown crystals (1.94 g, 71.3%), melting at 174—175°C and then solidyfying, followed by decomposition at 248°C. IR spectrum in the range 800—650 cm^{-1} (Nujol): 799, 773, 749 and 696 cm^{-1}.

Found: C, 55.99; H, 4.37; Pd, 17.63%; mol wt, 524. Calcd for $C_{28}H_{26}N_2O_2PdCl_2$: C, 56.06; H, 4.38; Pd, 17.74%; mol wt, 599.86. The less soluble compound in chloroform was obtained as yellow crystals, 0.26 g, mp 254—258°C dec. IR spectrum (Nujol): 1212 cm^{-1} ($CHCl_3$); 789, 770, 749, 723 and 699 cm^{-1} (in the range 800—650 cm^{-1}).

Found: C, 46.67; H, 3.41; N, 3.68; Cl, 13.19%. Calcd for $C_{28}H_{24}N_2O_2Pd_2Cl_2\cdot 1/8CHCl_3$: C, 46.21; H, 3.33; N, 3.82; Cl, 13.28%.

Reaction of *O*-Methyl Acetophenone Oxime with Lithium Tetrachloropalladate (II). In the same manner, we obtained 2.13 g (89.2%) of dichlorobis (*O*-methyl acetophenone oxime)palladium(II) as yellow crystals, mp 204°C dec.

Found: C, 45.62; H, 4.74; Pd, 22.07%; mol wt, 466. Calcd for $C_{18}H_{20}N_2O_2PdCl_2$: C, 45.44; H, 4.67; Pd, 22.37%; mol wt, 475.72.

Reaction of *O*-Acetyl and *O*-Benzoyl Acetophenone Oxime with Lithium Tetrachloropalladate (II). A methanol solution of 0.01 mol of each oxime was mixed with 20 m*l* of 0.5 M Li_2PdCl_4 in methanol. After standing for 20 hr, yellow crystals were formed and more solids were obtained by adding water. The yield of complex **7b** was about 80%. In the case of *O*-benzoyl acetophenone oxime, the filtrate was extracted with ether. After ether was removed, the residue was distilled *in vacuo* to give 0.88 g of colorless liquid. This was identified to be methyl benzoate by comparing its IR spectrum with that of an authentic sample.