BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 51 (11), 3407—3408 (1978)

The σ-Bonded Palladium(II) Complexes of 4-Chromanone Oxime Derivatives

Taeko IZUMI, Takao KATOU, Akira KASAHARA,* and Kaoru HANAYA,**
Department of Applied Chemistry, Faculty of Engineering, Yamagata University, Yonezawa 992
***Department of Chemistry, Faculty of Science, Yamagata University, Yamagata 990*

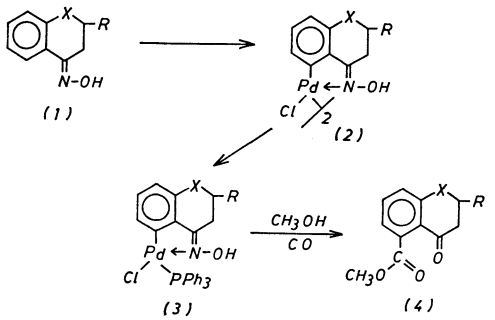
(Received May 22, 1978)

Synopsis. In the presence of sodium acetate, the reaction of 4-chromanone oxime with lithium tetrachloropalladate(II) affords an *ortho*-palladated binuclear complex. The reaction of the complex with carbon monoxide in methanol was also examined.

Following the first observation by Cope and Siekman[1] that azobenzene reacts with palladium(II) chloride to give an intramolecular *ortho*-palladation product with a carbon-to-metal σ-bond, considerable interest developed in this area.[2] Moreover, Onoue *et al.*[3] reported a reaction of aromatic ketoximes with palladium(II) chloride giving a dimeric σ-bonded complex. Herein, we wish to report on the *ortho*-metalation of 4-chromanone oxime (**1a**) with palladium(II) chloride and the reaction of the metalation product with carbon monoxide in methanol.

In the presence of sodium acetate, the reaction of **1a** with lithium tetrachloropalladate(II) in methanol gave a binuclear complex with palladium-carbon σ-bonding: di-μ-chloro-bis[4-chromanone oxime-5-*C*,*N*]dipalladium(II) (**2a**). Under the same conditions, flavanone oxime (**1b**) and 2-methyl-4*H*-1-benzothiopyran-4-one oxime (**1c**) also reacted with lithium tetrachloropalladate(II) to afford the *ortho*-palladated complexes, di-μ-chloro-bis[flavanone oxime-5-*C*,*N*]-dipalladium(II) (**2b**) and di-μ-chloro-bis[2-methyl-4*H*-1-benzothiopyran-4-one oxime-5-*C*,*N*]dipalladium-(II) (**2c**) respectively. On the basis of the microanalytical and spectroscopic data and the molecular weight, the **2a**—**c** complexes were shown to be intramolecularly *ortho*-palladated complexes. The molecular weights in chloroform are consistent with the values calculated for the binuclear complexes. The treatment of **2a**—**c** with triphenylphosphine gives results typical of a chlorine-bridged binuclear complex, affording the monomeric triphenylphosphine derivatives (**3a**—**c**). The IR spectra of **2a**—**c** showed the characteristic OH stretching frequency in the 3450—3350 cm^{-1} region and the characteristic deformation mode of 1,2,3-trisubstituted benzene at 790—785 cm^{-1} region, as shown in Table 1. Moreover, the C=N stretching frequency shifted to a slightly lower wave number (**2a**, 1635; **2b**, 1635; **2c**, 1620 cm^{-1}), characteristic of nitrogen lone-pair donation, as has been found for *ortho*-palladated aryloxime complexes.[3] In the far-infrared spectra of **2a**—**c** there are typicaly two bridged Pd–Cl stretching absorptions at 278—275 and 250—245 cm^{-1}. The NMR spectra of the **2a**—**c** complexes were in good agreement with the proposed structures. For example, the spectrum of **2a** has four bands: a triplet at 2.96 (J=6.0 Hz, 4H), a triplet at 4.24 (J=6.0 Hz, 4H), a multiplet at 6.60—7.40 (6H), and a broad singlet at 10.15 ppm (2H), the bands corresponding to $-CH_2-C=N$, $-O-CH_2-$, aromatic **H**, and **OH** respectively. These results and the IR spectral data show that one aromatic ring proton *ortho* to the C=N group was replaced by palladium(II). Similarly, the NMR spectra of **2b** and **2c** provide evidence for the occurrence of *ortho*-metalated aromatic rings (see Table 1).

The carbonylation of *ortho*-palladated products of azobenzene, Schiff bases, and tertiary benzylamines usually gives a variety of heterocyclic compounds.[4,5] In addition, it was found that benzophenone oxime gave 3-phenyl-1-isoindolinone by carbonylation in the presence of dicobalt octacarbonyl[6] or palladium(II) chloride in benzene.[3] We also studied the carbonylation of **2a**—**c** complexes. The attempted carbonylation of **2a**—**c** was unsuccessful, even at 100 °C; however, the triphenylphosphine derivatives, **3a**—**c**, in methanol were readily carbonylated at 100 °C to produce uncyclized and deoxymated esters (**4a**—**c**) in 28—45% yields. Maeda *et al.*[7] have recently shown that the C=N bond of ketoximes can be cleaved in the presence of the Pd(O) complex, with the subsequent formation of free ketone. The results of the carbonylation of **3a**—**c** complexes clearly suggest that a deoxymation of carbonylated intermediates with palladium species occurs.



1a, **2a**, **3a**, **4a**: R=H, X=O
1b, **2b**, **3b**, **4b**: R=Ph, X=O
1c, **2c**, **3c**, **4c**: R=CH_3, X=S

Fig. 1.

Experimental

Materials and Measurement. All the melting points are uncorrected. The **1a**[8] and **1b**[9] compounds were prepared by the method prevously reported. The **1c** compound (mp 136—138 °C) was prepared by the usual oxymation of the corresponding carbonyl compound. The IR spectra were measured on KBr disks (4000—650 cm^{-1}) or in nujol mulls mounted on thin polythene windows (700—200 cm^{-1}). The NMR spectra were observed in $CDCl_3$ or in DMSO-d_6 at 90 MHz, using TMS as the internal standard. The molecular weight was determined in $CHCl_3$, using a Hitachi 115

Table 1. The *ortho*-palladation of oximes (**1a—c**)

Oxime	Product (mp (dec), yield)	Found (Calcd) % and mol wt	IR and NMR (in DMSO-d_6) spectra
1a	**2a** (215—218 °C, 90%)	C, 35.27 (35.53) H, 2.51 (2.63) N, 4.48 (4.60) Mol wt 591 (608)	IR: 3400 (OH), 1635 (C=N), 790 (1,2,3-trisubstituted aromatic ring), 275 and 250 cm^{-1} (bridged Pd-Cl). NMR: δ 2.96 (t, 4H, -CH_2-C=N), 4.24 (t, 4H, -O-CH_2-), 6.60—7.40 (m, 6H, aromatic **H**), and 10.15 ppm (br s, 2H, **OH**).
1b	**2b** (260—265 °C, 82%)	C, 47.25 (47.38) H, 2.93 (3.15) N, 3.29 (3.42) Mol wt 748 (760)	IR: 3450 (OH), 1635 (C=N), 790 (1,2,3-trisubstituted aromatic ring), 275 and 245 cm^{-1} (bridged Pd-Cl). NMR: δ 2.58—3.45 (m, 4H, -CH_2-C=N), 5.25 (d-d, 2H, -O-C**H**-), 6.60—7.81 (m, 16H, aromatic **H**), and 10.60 ppm (s, 2H, **OH**).
1c	**2c** (228—230 °C, 90%)	C, 35.78 (35.90) H, 2.83 (2.99) N, 4.06 (4.19) Mol wt 650 (668)	IR: 3350 (OH), 1620 (C=N), 785 (1,2,3-trisubstituted aromatic ring), 278 and 245 cm^{-1} (bridged Pd-Cl). NMR: δ 1.28 (d, 6H, -CH_3), 2.55—3.33 (m, 4H, -CH_2-C=N), 4.85 (m, 2H, S-C**H**-), 6.68—7.55 (m, 6H, aromatic **H**), and 10.45 ppm (br s, 2H, **OH**).

Table 2. The triphenylphosphine derivatives (**3a—c**)

Complex	Mp (dec) (yield)	Found (Calcd) % and mol wt	IR and NMR (in $CDCl_3$) spectra
3a	214—215 °C (70%)	C, 57.08 (57.25) H, 3.91 (4.06) N, 2.27 (2.47) Mol wt 548 (566)	IR: 3200 (OH), 1640 (C=N), 790 (1,2,3-trisubstituted aromatic ring), 305 cm^{-1} (terminal Pd-Cl). NMR: δ 3.05 (t, J=6.0 Hz, 2H, -CH_2-C=N), 4.25 (t, J=6.0 Hz, 2H, -O-CH_2-), 6.00—6.50 (m, 3H, aromatic **H**), 7.50)m, 15H, aromatic **H**), and 10.40 ppm (br s, 1H, **OH**).
3b	210—212 °C (75%)	C, 61.55 (61.69) H, 3.97 (4.20) N, 2.03 (2.18) Mol wt 625 (642)	IR: 3200 (OH), 1640 (C=N), 790, 740, 690 (aromatic ring), and 305 cm^{-1} (terminal Pd-Cl). NMR: δ 3.04 (d-d, J=17 and 12 Hz, 1H, -C**H**-C=N), 3.65 (d-d, J=17 and 3.5 Hz, 1H, -C**H**-C=N), 5.10 (d-d, J=12 and 3.5 Hz, 1H, O-C**H**-), 6.05 (m, 1H, aromatic **H**), 6.60 (m, 2H, aromatic **H**), 7.60 (m, 20H, aromatic **H**), and 10.50 ppm (br s, 1H, **OH**).
3c	208—210 °C (65%)	C, 56.16 (56.38) H, 4.05 (4.19) N, 2.27 (2.36) Mol wt 585 (596)	IR: 3200 (OH), 1640 (C=N), 785 (1,2,3-trisubstituted aromatic ring), and 310 cm^{-1} (terminal Pd-Cl). NMR: δ 1.25 (d, 3H, -CH_3), 2.97 (d-d, J=16 and 12 Hz, 1H, -C**H**-C=N), 3.55 (d-d, J=16 and 4 Hz, 1H, -C**H**-C=N), 4.68 (m, J=12 and 4 Hz, 1H, -C**H**-O), 6.11—6.58 (m, 3H, aromatic **H**), 7.50 (m, 15 H, aromatic **H**), and 10.40 ppm (br s, 1H, **OH**).

Table 3. The carbonylation products (**4a—c**)

Compound	Mp (yield)	Found (Calcd) % and mol wt	IR, NMR (in $CDCl_3$), and MS spectra
4a	38—40 °C (45%)	C, 63.38 (63.45) H, 5.88 (5.81) Mol wt (208)	IR: 1735 (ester), 1695 (C=O), 785 cm^{-1} (1,2,3-trisubstituted aromatic ring). NMR: δ 2.82 (t, 2H, -CH_2C=O), 3.94 (s, 3H, -COOCH_3), 4.56 (t, 2H, -CH_2-O), 7.05 (m, 2H, aromatic **H**), and 7.45 ppm (m, 1H, aromatic **H**). MS: *m/e* 208 (M^+).
4b	44—46 °C (28%)	C, 72.21 (72.33) H, 4.86 (5.00) Mol wt (282)	IR: 1735 (ester), 1695 (C=O), 790, 740, and 690 cm^{-1} (aromatic ring). NMR: δ 2.96 (m, 2H, -CH_2-CO), 3.93 (s, 3H, -COOCH_3), 5.48 (d-d, 1H, -O-C**H**-), and 6.98—7.90 ppm (m, 8H, aromatic **H**). MS: *m/e* 282 (M^+).
4c	50—52 °C (32%)	C, 60.95 (61.01) H, 5.03 (5.12) Mol wt (236)	IR: 1735 (ester), 1695 (C=O), 790 cm^{-1} (1,2,3-trisubstituted aromatic ring). NMR: δ 1.26 (d, 3H, -CH_3), 2.78 (m, 2H, -CH_2-CO), 3.87 (s, 3H, -COOCH_3), 4.78 (m, 1H, -C**H**-O-), and 7.01—7.54 ppm (m, 3H, aromatic **H**). MS: *m/e* 236 (M^+).

vapor-pressure osmometer.

General Procedure of the Preparation of Complexes ***2a—c.*** A solution of 5 mmol of the **1a—c** oximes in methanol (50 ml) was added to a mixture of lithium tetrachloropalladate (II) (1.31 g, 5 mmol) and sodium acetate trihydrate (0.68 g, 5 mmol) in methanol (50 ml). The resulting mixture was stirred for 24 h at room temperature. The pale yellow precipitate thus formed was filtered off and purified by recrystallization from chloroform-hexane or by column chromatography (SiO_2–$CHCl_3$). The results are listed in Table 1.

General Procedure for the Preparation of Triphenylphosphine Derivatives ***3a—c.*** Triphenylphosphine (0.26 g, 1 mmol) and the **2a—c** complexes (0.5 mmol) were dissolved in benzene, and then the mixture was stirred for 6 h at room temperature. The solvent was removed under reduced pressure, and the products were obtained as pale yellow crystals from chloroform-hexane. The results are summarized in Table 2.

The Carbonylation of The ***3a—c*** *Complexes.* In 50 ml of methanol, the **3a—c** complexes were carbonylated at 100 °C under a carbon monoxide pressure of 60 atm for 20 h with shaking. The product was then isolated by filtering to remove a precipitated palladium and distilling under reduced pressure to remove the solvent. The residue was dissolved in hexane or benzene and chromatographed on silica gel to afford colorless crystals, which can be identified as 5-methoxycarbonyl derivatives (**4a—c**). The results are summarized in Table 3.

References

1) A. C. Cope and R. W. Siekman, *J. Am. Chem. Soc.*, **87**, 3272 (1965).
2) P. M. Maitlis, "The Organic Chemistry of Palladium," Academic Press, New York (1971), Vol. 1, p. 82; J. Tsuji, *Yuki Gosei Kagaku Kyokai Shi*, **35**, 10 (1977).
3) H. Onoue, K. Minami, and K. Nakagawa, *Bull. Chem. Soc. Jpn.*, **43**, 3480 (1970).
4) H. Takahashi and J. Tsuji, *J. Organometal. Chem.*, **10**, 511 (1967).
5) J. M. Thompson and R. F. Heck, *J. Org. Chem.*, **40**, 2667 (1975).
6) A. Rosenthal, R. F. Astbury, and A. Hubscher, *J. Org. Chem.*, **33**, 1037 (1958).
7) K. Maeda, I. Moritani, T. Hosikawa, and S.-I. Murahashi, *Tetrahedron Lett.*, **1974**, 797.
8) A. Arndt and G. Kallner, *Ber.*, **57**, 202 (1924).
9) A. Kasahara, *Nippon Kagaku Zasshi*, **80**, 416 (1959).