BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 2887—2888 (1973)

Some Palladium Complexes Containing a Benzoyl Group

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(Received February 27, 1973)

The acyl complexes of transition metals are prepared by the reaction of acyl halides with low-oxidation transition metal complexes or by the insertion of CO into the metal-carbon bond of alkyl or aryl complexes. The formation of the complexes containing a benzoyl group have also been reported in several papers.[1–4] However, no palladium complex with a benzoyl group has yet been prepared. In this paper we will report on the formation and the infrared spectra of $PdCl(COPh)(PPh_3)_2$ (I) and other benzoyl complexes of palladium derived from (I) by ligand-exchange reactions.

Results and Discussion

The reaction of $Pd(PPh_3)_4$ with PhCOX gave $PdX(COPh)(PPh_3)_2$ (X=Cl, Br). The recrystallization of the chloride (I) from acetone gave (I′) containing one molecule of acetone. Two other complexes, PdCl(COPh)(P–P) (III) and PdCl(COPh)(phen) (IV) (P–P=$Ph_2PCH_2CH_2PPh_2$, phen=*o*-phenanthroline), were obtained by the ligand-exchange reaction of (I). In the solid state, all the complexes are stable enough to handle in air, but are unstable in solution. The reaction of (I) with dipyridyl did not give the expected compound, PdCl(COPh)(dipy). This failure might be due to the fact that the ligand exists in the *trans* form in the free state.

Table 1. IR data of the palladium complexes (cm^{-1})

	Complex	ν(C=O)	ν(Pd–Cl)
(I)	$PdCl(COPh)(PPh_3)_2$	1640	235
(I′)	$PdCl(COPh)(PPh_3)_2(CH_3)_2CO$	1702 1648	235
(II)	$PdBr(COPh)(PPh_3)_2$	1640	—
(III)	PdCl(COPh)(P–P)	1639	282
(IV)	PdCl(COPh)(phen)	1643	325

The infrared data of the complexes prepared are summarized in Table 1. As is clear from the table, all the complexes have a strong band due to ν(CO) *ca.* 1640 cm^{-1}, this is characteristic of a benzoyl group coordinated to a transition metal. The –C=O stretching frequency has been lowered *ca.* 80 cm^{-1} in comparison with the ν(CO) of the free benzoyl chloride. Green[5] suggested that the lowering may be due either to some double bonding of the metal with π-orbitals of the C=O group or to some direct interaction of the metal with the C=O group. In the ^{13}C NMR of $Fe(CO)_2(\pi\text{-}C_5H_5)(COPh)$,[6] the resonance of $^{13}COPh$ showed a large low-field shift which could be associated with the multiple bonding between the *d*-orbitals of the metal and the sp^2 carbon atom. Therefore, it was expected that the change in the donor atom *trans*

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4) M. Kubota and D. M. Blake, *J. Amer. Chem. Soc.*, **93**, 1368 (1971).

5) G. E. Coates, M. L. H. Green, and K. Wada, "Organometallic Compounds," Vol. 2, Methuen, London, (1968) p. 261.

6) J. A. Connor, E. M. Jones, E. W. Randall, and E. Rosenberg, *J. Chem. Soc. A*, **1972**, 2419.

to the benzoyl group has some effect on the ν(CO) of the ligand. However, the ν(CO) values of the complexes studied here remained approximately constant. Although the results may be explained by assuming either that the difference in the π-acceptor property of the donor atom is small[7] or that the direct interaction between the metal and the CO group is important, further investigations seem to be necessary to examine the effect of π-interaction on the ν(CO) of the acyl group.

In (I′), the band due to the ν(CO) of acetone was observed at 1702 cm^{-1}. The band is shifted *ca.* 30 cm^{-1} to wave numbers lower than that of free acetone. However, this shift is smaller than the lowering of ν(CO) found for the acetone which coordinates to Rh through a lone pair on the oxygen.[8] Thus, it seems to be difficult to discuss the coordination of acetone for (I′) on the basis of the ν(CO) data alone.

The far infrared spectrum of (I) showed three bands, at 317, 270, and 235 cm^{-1}. The two bands at 270 and 235 cm^{-1} disappeared in the corresponding bromide. Since the ν(Pd–Cl) of (III), where P is *trans* to Cl, appeared at 281 cm^{-1}, one possible explanation of the disappearance of the band at 270 cm^{-1} is to assume the presence of the *cis*-isomer. However, its existence is rather suspected when the steric hindrance of the two bulky groups (PPh$_3$) in the *cis*-position is considered. Thus, the assignment of the band at 270 cm^{-1} is uncertain at present. Probably ^{31}P NMR measurements would clarify the ambiguity.

Recently Dent *et al.*[9] reported that the assignment of ν(Pt–Cl) for PtCl(COPh)(PPh$_3$)$_2$ made by Baired and Wilkinson[1] was incorrect and that the ν(Pt–Cl) really appeared at 261 cm^{-1}, indicating a large *trans* influence of an acyl group. This is also true in iridium complexes.[4,10] The large *trans* influence of an acyl group seems to be a general tendency, and the band at 235 cm^{-1} of (I) is probably due to the ν(Pd–Cl), where Cl is *trans* to the benzoyl group.

Experimental

Measurements. The infrared spectra were recorded with JASCO-DS-402G and HITACHI EPI-L2 spectrometers (nujol or HCB mulls).

Materials. The Pd(PPh$_3$)$_4$ was prepared by the method described in the literature.[11] The benzoyl chloride and benzoyl bromide were distilled before use. All the solvents used were dried over sodium and distilled under nitrogen. All the reactions were carried out under nitrogen.

Chloro(benzoyl)bis(triphenylphosphine)palladium (I): Into 0.9 g of Pd(PPh$_3$)$_4$ in 100 ml of benzene, we stirred 0.5 ml of C_6H_5COCl in 50 ml of benzene. After the yellow solution had then been allowed to be stirred overnight, it was concentrated to about 30 ml and filtered off to remove the small amount of precipitates formed. The filtrate was subsequently treated with 150 ml of ether. The pale yellow precipitates were filtered, washed with ether, and dried *in vacuo*. Found: C, 66.4; H, 4.9; Pd, 13.6%. Calcd for $C_{43}H_{35}ClOP_2Pd$: C, 66.9; H, 4.6; Pd, 13.8%.

The recrystallization of (I) from acetone gave PdCl(COPh)(PPh$_3$)$_2$(CH$_3$)$_2$CO, (I′). Found: C, 66.7; H, 4.9; Pd, 12.8%. Calcd for $C_{46}H_{41}ClO_2P_2Pd$: C, 66.6; H, 5.0; Pd, 12.8%.

Similarly, PdBr(COPh)(PPh$_3$)$_2$ (II) was prepared by the reaction of Pd(PPh$_3$)$_4$ with benzoyl bromide. Found: C, 62.5; H, 4.2; Pd, 12.9%. Calcd for $C_{43}H_{35}BrOP_2Pd$: C, 63.3; H, 4.3; Pd, 13.0%.

Chloro(benzoyl)1,2-bis(diphenylphosphino)ethanepalladium (III): To 1 g of PdCl(COPh)(PPh$_3$)$_2$ in 100 ml of benzene, we added 0.5 g of $Ph_2PCH_2CH_2PPh_2$ in 10 ml of benzene. About ten minutes later, yellow crystals started to precipitate. After the mixture had been stirred for 1 hr, the crystals were filtered off, washed with ether, and dried *in vacuo*. Found: C, 61.7; H, 4.6; Pd, 15.9%. Calcd for $C_{33}H_{29}ClOP_2Pd$: C, 61.4; H, 4.5; Pd, 16.5%.

Chloro(benzoyl)(*o*-phenanthroline)palladium (IV) was prepared in a similar way. Found: C, 53.1; H, 3.1; Pd, 24.5; N, 6.7%. Calcd for $C_{19}H_{13}N_2ClOPd$: C, 53.4; H, 3.1; Pd, 24.9; N, 6.7%.

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