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Oxidative Additions of Alkyl Halides to Palladium(0) Carbonyl Complex

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Oxidative addition reactions of alkyl halides to $Pd(CO)(PPh_3)_3$ were studied. Vinyl chloride, allyl chloride, allyl bromide, methallyl chloride, benzyl bromide, methyl iodide, and iodobenzene react with $Pd(CO)(PPh_3)_3$ to afford the corresponding acyl complexes of the type *trans*-$PdX(COR)(PPh_3)_2$. The reactions proceed rapidly when the dissociation energy of carbon-halogen bond in the saturated alkyl halides is smaller than about 60 kcal/mol. In the case of the unsaturated alkyl halides the more inert carbon-halogen bond can be activated by initial formation of π complexes.

Oxidative addition reactions to lower valent metal complexes are currently drawing considerable attention in relation to transition metal catalysis. The reactions with alkyl compounds often give products possessing stable metal-carbon σ bonds.

So far the acyl complexes of palladium(II) of the type *trans*-$PdX(COR')(PR_3)_2$ reported have been limited to acetyl or benzoyl complexes such as *trans*-$PdCl(COMe)(PPh_3)_2$ prepared by oxidative addition of acetyl chloride to $Pd(PPh_3)_4$[1] and *trans*-$PdX(COR)(PEt_3)_2$ (R=Me or Ph) prepared by carbonylation of *trans*-$PdX(R)(PEt_3)_2$.[2] We found that oxidative addition of alkyl halides to $Pd(CO)(PPh_3)_3$ gives the acyl complexes of this type.[3] In this paper we wish to report the reactivity of various alkyl halides towords $Pd(CO)(PPh_3)_3$.

Results and Discussion

Reactions were carried out by addition of excess alkyl halides to toluene solutions containing $Pd(CO)(PPh_3)_3$ under carbon monoxide at 1 atm. Immediate reaction took place, the original yellow color of the solutions paled and the solutions were stirred for 1—2 hr at ambient temperature for completion of the reactions. After addition of *n*-hexane to the solutions, the acyl complexes were obtained.

Among the alkyl halides examined, allyl chloride, allyl bromide, methallyl chloride, benzyl bromide, and iodobenzene react with the carbonyl complex rapidly, giving the corresponding acyl complexes of the type *trans*-$PdX(COR)(PPh_3)_2$ in high yields.

$$Pd(CO)(PPh_3)_3 + R\text{-}X \longrightarrow PdX(COR)(PPh_3)_2$$

Methyl iodide gave two isomers of methyl complexes in addition to the expected acetyl complex. Vinyl chloride is less reactive and the oxidative addition product was obtained in a poor yield.[3] Other alkyl halides such as PhBr, $PhCH_2Cl$, MeBr, EtI, EtBr, *n*-PrCl, *n*-PrBr, *i*-PrCl, *i*-PrBr, $CCl_2{=}CCl_2$ or *cis*-CHCl=CHCl did not react, the carbonyl complex being recovered.

The reactivity of alkyl halides decreased in the order iodide>bromide>chloride, and allyl≈methallyl>benzyl>phenyl≈methyl>vinyl>propyl≈ethyl. In a series of alkyl chlorides, allyl, and methallyl chlorides give the acyl complexes in high yields but not benzyl chloride. Benzyl bromide gives the acyl com-

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[1] P. Fitton, M. P. Johnson, and J. E. McKeon, *Chem. Commun.*, **1968**, 6.

[2] G. Booth and J. Chatt, *J. Chem. Soc., A*, **1966**, 634.

[3] K. Kudo, M. Hidai, and Y. Uchida, *J. Organometal. Chem.*, **33**, 393 (1971).

Table 1. Formation of $PdX(COR)(PPh_3)_2$

R	Cl		Br		I	
	Yield %	Ed	Yield %	Ed	Yield %	Ed
CH_2=CH–	12[a]	85.5	—	73.4	—	
CH_2=$CHCH_2$–	82[a]	60	95	46	—	36
CH_2=$CMeCH_2$–	91	70	—		—	
$PhCH_2$–	X[b]		81	51	—	39
Me–	—	80	X[b]	67	26[a,c]	54
Ph–	—		X[b]	71	95	61

a) Quoted from Ref. 3.
b) No reaction occurred.
c) $PdI(Me)(PPh_3)_2$ (2 isomers) were also obtained(30%).

plex, whereas in the case of methyl and phenyl halides only iodides react with the carbonyl complex. The reaction of vinyl chloride gives the acyl complex in a poor yield. No reaction takes place in the case of propyl and ethyl halides. This is in line with the increase of the dissociation energy (Ed) of the carbon-halogen bond in alkyl halides (Table 1). The reaction of the saturated alkyl halides proceeds rapidly when Ed is smaller than about 60 kcal/mol. Unsaturated compounds which have larger Ed undergo oxidative additions. For example, methallyl chloride undergoes reaction, though Ed is 70 kcal/mol, comparable to that of methyl and phenyl bromides which do not undergo oxidative addition. Even more inert vinyl chloride (Ed=85.5 kcal/mol) gives $PdCl(COCH{=}CH_2)(PPh_3)_2$, though in a poor yield. This may be explained by the initial coordination of the unsaturated compounds to palladium through a π-bonding, which would cause the activation of the carbon-halogen bond, followed by isomerization to the acyl complexes.

In these oxidative addition reactions to zero-valent palladium complexes, the dissociated species are generally considered to be active species. Since $Pd(CO)(PPh_3)_3$ dissociates to a coordinatively unsaturated species $[Pd(CO)(PPh_3)_2]$ in solution,[3] the reaction probably proceeds according to the following scheme:

$$Pd(CO)(PPh_3)_3 \rightleftarrows [Pd(CO)(PPh_3)_2] + PPh_3 \xrightarrow{R\text{-}X}$$
$$[PdX(R)(CO)(PPh_3)_2] \longrightarrow PdX(COR)(PPh_3)_2$$

The unsaturated species $[Pd(CO)(PPh_3)_2]$ is susceptible to electrophilic attack by alkyl halides, giving the unstable five-coordinate palladium(II) carbonyl complex $[PdX(R)(CO)(PPh_3)_2]$. An immediate insertion of the carbonyl ligand into the palladium-alkyl bond may occur to produce the acyl complexes $Pd(COR)X(PPh_3)_2$. The alkenyl halides initially react with the coordinatively unsaturated species $[Pd(CO)(PPh_3)_2]$ to form π complexes $[Pd(C{=}C)(CO)(PPh_3)_2]$, followed by isomerization to the acyl complexes. This is supported by the fact that vinyl chloride reacts with $Pd(PPh_3)_4$ affording an unstable π-complex.[4] The reaction mechanism involving the initial formation of alkyl complexes $PdX(R)(PPh_3)_2$ followed by carbonylation with atmospheric carbon monoxide is reasonably excluded for the following reasons: the acetyl complex could be obtained by a reaction of methyl iodide under nitrogen atmosphere, and Booth and Chatt reported that carbonylation of the aromatic phosphine complexes of palladium-alkyl was unsuccesful.[2]

The acyl complexes obtained here are stable in an inert atmosphere. It is reasonable that they have a *trans*-structure in analogy with $PdCl(COCH_2CH{=}CH_2)(PPh_3)_2$ which shows ν(Pd–Cl) at 320 cm^{-1} corresponding to a *trans*-square planar. It is known that the *trans*-isomer is more stable in these palladium(II) phosphine complexes than the *cis*, especially in the presence of excess triphenylphosphine.[1]

Table 2. IR data and decomposition points of *trans*-$PdX(COR)L_2$ ($L{=}PPh_3$)

Complex	ν(C=O)	ν(C=C) cm^{-1}	°C
$PdCl(COCH{=}CH_2)L_2$	1665	1620	—
$PdCl(COCH_2CH{=}CH_2)L_2$	1675	1636	115
$PdBr(COCH_2CH{=}CH_2)L_2$	1687	1640	—
$PdBr(COCH{=}CHCH_3)L_2$	1680	1634	—
$PdCl(COCH_2CMe{=}CH_2)L_2$	1695	1647	70
$PdBr(COCH_2Ph)L_2$	1696	—	105
$PdI(COMe)L_2$	1690	—	141
$PdI(COPh)L_2$	1634	—	107

IR spectra of the acyl complexes show a strong absorption at 1700—1630 cm^{-1}, assignable to C=O stretching (Table 2). The low shift of ν(C=O) for the benzoyl complex may be attributed to the conjugation between the caronyl group and phenyl ring. A slight conjugation between the carbonyl group and the carbon-carbon double bond is observed in the acryloyl complex obtained by the reaction of vinyl chloride. The product from allyl chloride exhibits absorptions at 1675 and 1636 cm^{-1} assignable to ν(C=O) and ν(C=C), respectively. Deformations of terminal vinyl group occur at 990 and 905 cm^{-1}, indicating that the complex is 3-butenoyl complex $PdCl(COCH_2CH{=}CH_2)(PPh_3)_2$. On the other hand, the product from allyl bromide shows ν(C=O) at 1687 and 1680 cm^{-1} and ν(C=C) at 1640 and 1634 cm^{-1}, respectively, indicating the formation of two isomers, presumably 2- and 3-butenoyl complexes. The absorption bands at 1680 and 1634 cm^{-1} are assignable to 2-butenoyl complex $PdBr(COCH{=}CHCH_3)(PPh_3)_2$, since the slight conjugation between C=O and C=C groups is expected to shift the bands to lower region. Separation of the two isomers was unsuccessful. The relationship between ν(C=O) and thermal stability of the acyl complexes was not observed. This may be explained by the fact that contribution of back donation from palladium to acyl group to stability is small, though the back donation is expected to strengthen the palladium-acyl bond and be reflected in ν(C=O).

Experimental

IR spectra were recorded as Nujol mulls on a JASCO DS-403 spectrophotometer. Decomposition points were measured in an argon atmosphere and are uncorrected. $Pd(CO)(PPh_3)_3$ was prepared according to Method B in literature.[3]

Reaction of Methallyl Chloride. 0.12 ml of methallyl

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[4] P. Fitton and J. E. McKeon, *Chem. Commun.*, **1968**, 4.

chloride was added through a syringe to a toluene solution (3 ml) containing 0.12 g of $Pd(CO)(PPh_3)_3$ at −10°. The solution immediately turned from orange-yellow to pale yellow. It was stirred for 2 hr at ambient temperature, during which course of time 0.085 g (91%) of *trans*-$PdCl(COCH_2CMe{=}CH_2)(PPh_3)_2$ precipitated. Decomp. 70 °C. Found: C, 65.6; H, 4.8%. Calcd for $C_{41}H_{37}OClP_2Pd$: C, 65.7; H, 5.0%.

Reaction of Allyl Bromide. A mixture of *trans*-$PdBr(COCH_2CH{=}CH_2)(PPh_3)_2$ and *trans*-$PdBr(COCH{=}CHCH_3)(PPh_3)_2$ (0.069 g; 95%) was obtained analogously from 0.086 g of $Pd(CO)(PPh_3)_3$ and 0.08 ml of allyl bromide in 3 ml of toluene. Found: C, 60.2; H, 4.7%. Calcd for $C_{40}H_{35}OBrP_2Pd$: C, 61.6; H, 4.5%.

Reaction of Benzyl Bromide. 0.10 g (81%) of *trans*-$PdBr(COCH_2Ph)(PPh_3)_2$ was obtained from 0.14 g of $Pd(CO)(PPh_3)_3$ and 0.18 ml of benzyl bromide in 3 ml of toluene. Decomp. 105 °C. Found: C, 64.1; H, 5.0%. Calcd for $C_{44}H_{37}OBrP_2Pd$: C, 63.7; H, 4.5%.

Reaction of Iodobenzene. 0.056 g (95%) of *trans*-$PdI(COPh)(PPh_3)_2$ was obtained from 0.063 g of $Pd(CO)(PPh_3)_3$ and 0.08 ml of iodobenzene in 3 ml of toluene. Decomp. 107 °C. Found: C, 59.6; H, 3.9%. Calcd for $C_{43}H_{35}OIP_2Pd$: C, 59.8; H, 4.1%.