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New β-Carbonylvinylpalladium(II) Complexes Derived from 2-Chlorovinyl Ketones and Tetrakis(triphenylphosphine)palladium(0)

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Chloro(*trans*-3-oxo-3-phenyl-1-propenyl)bis(triphenylphosphine)palladium(II), chloro(*trans*-3-oxo-3-*p*-tolyl-1-propenyl)bis(triphenylphosphine)palladium(II), chloro(3-oxo-1-cyclohexenyl)bis(triphenylphosphine)palladium(II), and chloro(5,5-dimethyl-3-oxo-1-cyclohexenyl)bis(triphenylphosphine)palladium(II) were prepared by reactions between $Pd(PPh_3)_4$ and linear or cyclic 2-chlorovinyl ketones. The halogen metathesis reactions with LiBr yielded the corresponding bromo complexes. Each of the β-carbonylvinyl groups in these eight complexes was found to be situated at the *trans* position to a palladium-halogen bond, on the basis of IR and ^{1}H-NMR studies. The complexes with the cyclic β-carbonylvinyl groups were rather stable. The oxidative addition of linear 2-chlorovinyl ketones proceeded with retention of configuration about the double bond.

Several investigations have been reported on the oxidative addition of vinyl halides, for example, polyhalogenated olefins,[1] fluorovinyl halides,[2] and some styryl halide derivatives[3] with a tris- or tetrakis(tertiary phosphine)platinum(0) complex. A few halogeno-substituted vinylpalladium(II) complexes have been obtained by the reactions of $[Pd(PPh_3)_4]$ with polyhalogenated olefins[4] or fluorovinyl halides.[5] Moreover, Murahashi *et al.*[6] reported cross-coupling reactions of vinyl halides with alkyl magnesium bromide catalysed by $[Pd(PPh_3)_4]$, *via* the oxidative addition.

Although 2-chlorovinyl ketones are very reactive and useful intermediates for the syntheses of some organic compounds,[7] only a few investigations have been reported concerning the reactions between linear 2-chlorovinyl ketones and iron,[8] tungsten,[9] or rhenium[10] carbonyl derivatives.

We have been interested in the ease of carbon-chlorine bond cleavage in the linear and cyclic chloro olefins activated by electron-withdrawing acyl groups. In the present research, 2-chlorovinyl ketones were found to react with $[Pd(PPh_3)_4]$ to yield several new β-carbonylvinylpalladium(II) complexes, and some properties of these complexes were studied.

Experimental

General Procedures. IR spectra were obtained using a Hitachi 285 grating spectrometer and a Shimadzu IR 450 spectrometer. ^{1}H-NMR spectra were run on a Japan Electron Optics Laboratory JNM-MH-100 spectrometer. Melting points were determined on a Yanagimoto MP-S3 microstage apparatus in capillary tubes in dinitrogen and are uncorrected.

Phenyl 2-chlorovinyl ketone,[7,11] *p*-tolyl 2-chlorovinyl ketone,[7,12] 3-chloro-2-cyclohexen-1-one,[13] and 3-chloro-5,5-dimethyl-2-cyclohexen-1-one[14] were prepared according to the methods described in the literature. Solvents were dried and distilled by the usual methods, and all operations were performed in an atmosphere of dry dinitrogen.

Reactions of the Linear 2-Chlorovinyl Ketones with $Pd(PPh_3)_4$. Phenyl 2-chlorovinyl ketone (0.60 g) in 8 ml of benzene was added dropwise to a suspension of $Pd(PPh_3)_4$ (3.40 g) in 25 ml of benzene, and the mixture was stirred at room temperature for two days. Benzene was removed *in vacuo* from the suspension, and the residue was extracted with dichloromethane. The extract was evaporated to dryness and the resulting solid was washed with acetone, ethanol, and diethyl ether to yield chloro(*trans*-3-oxo-3-phenyl-1-propenyl)bis(triphenylphosphine)palladium (II) (**1**), 0.56 g.

Chloro(*trans*-3-oxo-3-*p*-tolyl-1-propenyl)bis(triphenylphosphine)palladium(II) (**2**) was obtained similarly.

Reactions of the Cyclic 2-Chlorovinyl Ketones with $Pd(PPh_3)_4$. A mixture of $Pd(PPh_3)_4$ (3.10 g) and 3-chloro-2-cyclohexen-1-one (0.71 g) in 25 ml of benzene was warmed at *ca.* 60 °C for 3 h. The solvent was removed *in vacuo* and the resulting residue was recrystallized from benzene to give a pale yellow powder of chloro(3-oxo-1-cyclohexenyl)bis(triphenylphosphine)palladium(II) (**3**), 1.71 g.

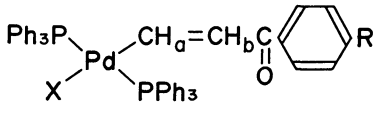
Chloro(5,5-dimethyl-3-oxo-1-cyclohexenyl)bis(triphenylphosphine)palladium(II) (**4**) was prepared by a similar method.

*Halogen Metathesis Reactions of **1**, **2**, **3**, and **4**.* The complex **1** (0.25 g) and LiBr (0.05 g) were mixed in 12 ml of acetone and the suspension was stirred at room temperature for four days. The resulting precipitate was collected and washed with acetone, ethanol, and diethyl ether to yield a pale yellow powder of bromo(*trans*-3-oxo-3-phenyl-1-propenyl)bis(triphenylphosphine)palladium(II) (**5**), 0.07 g.

Bromo(*trans*-3-oxo-3-*p*-tolyl-1-propenyl)bis(triphenylphosphine)palladium(II) (**6**), bromo(3-oxo-1-cyclohexenyl)bis(triphenylphosphine)palladium(II) (**7**), and bromo(5,5-dimethyl-3-oxo-1-cyclohexenyl)bis(triphenylphosphine)palladium(II) (**8**) were prepared by a method similar to **5**.

Results and Discussion

Four new β-carbonylvinylpalladium(II) complexes: **1**, **2**, **3**, and **4**, were obtained from the oxidative addition reaction between $Pd(PPh_3)_4$ and 2-chlorovinyl ketones. The halogen metathesis reaction with lithium bromide yielded the corresponding bromo complexes: **5**, **6**, **7**, and **8**. The cyclic 2-chlorovinyl ketones, such as 3-chloro-2-cyclohexen-1-one, were more thermally unstable and sensitive to moisture than the linear ketones. However, the reaction of the cyclic ketones

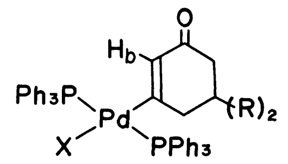


1 ; R = H , X = Cl
2 ; R = CH₃ , X = Cl
5 ; R = H , X = Br
6 ; R = CH₃ , X = Br

Table 1. Yields and properties of the palladium complexes

Complex	Yield (%)	Mp (°C)[a]	Color	C (%) Calcd	C (%) Found	H (%) Calcd	H (%) Found
1	24	>112	Pale yellow	67.77	67.73	4.68	4.66
2	31	>126	Pale yellow	68.07	67.91	4.84	4.79
3	84	>191	Pale yellow	66.24	66.61	4.90	4.95
4	28	>146	Off white	66.93	67.03	5.23	5.44
5	27	>116	Pale yellow	64.19	64.66	4.43	4.52
6	41	>127	Off white	64.54	64.23	4.59	4.56
7	66	>118	Pale yellow	62.59	62.91	4.63	4.66
8	81	>179	Pale yellow	63.36	63.37	4.96	5.06

a) With decomposition in dinitrogen.



3 ; R = H , X = Cl
4 ; R = CH3 , X = Cl
7 ; R = H , X = Br
8 ; R = CH3 , X = Br

Table 2. Characteristic IR bands of the complexes[a]

Complex	ν(C=O)	ν(C=C)	ν(Pd–Cl)
1	1650	1533	290
2	1642	1517	280
3	1640	1540	280
4	1645	1560	285
5	1648	1530	—
6	1642	1517	—
7	1630	1540	—
8	1635	1555	—

a) Measured in KBr disc, values in cm^{-1}.

with $Pd(PPh_3)_4$ took place only at temperatures above 50 °C, while that of the linear ketones proceeded smoothly at room temperature. When the solvents were not sufficiently dried, the complexes with the linear β-carbonylvinyl groups decomposed partially and turned brown. Yields, analytical data, and the properties of the eight complexes prepared are summarized in Tables 1, 2, and 3. These complexes were readily soluble in dichloromethane and hot benzene, and the complexes with the linear β-carbonylvinyl groups were also moderately soluble in benzene at room temperature.

The complexes obtained in this study possess a palladium-vinyl σ bond, judging from the halogen metathesis reaction and the existence of ν(Pd–Cl) bands shown in Table 2.

The ν(C=C) stretching frequencies of all the complexes were lowered about 45—80 cm^{-1} relative to those of the starting 2-chlorovinyl ketones. These lowering shifts of the ν(C=C) frequencies were probably associated with some double-bonding character between the d orbitals of palladium and the sp^2 carbon atom. The ν(C=O) stretching frequencies of the complexes with the cyclic β-carbonylvinyl groups were shifted by 25—60 cm^{-1} towards lower wavenumbers, relative to those of the starting ketones. The lowering shifts of the ν(C=O) frequencies were possibly due to an extension of the π-conjugation through the β-carbonylvinylpalladium moiety. On the other hand, the complexes with the linear β-carbonylvinyl groups showed small lowering shifts (*ca.* 10 cm^{-1}) of the ν(C=O) frequencies, in comparison with the starting 2-chlorovinyl ketones. This fact might correspond to a small degree of additional

Table 3. ^1H-NMR data of the palladium complexes[a,b]

Complex	H_b δ, ppm	H_b J_{PH}, Hz	H_b J_{ab}, Hz	CH_3 δ, ppm	$-CH_2-$ δ, ppm
1	6.17(dt)	2.1	15.5	—	—
2	6.15(dt)	2.3	18.0	2.31(s)	—
3	6.18(t)	2.2	—	—	0.54(m), 1.28(t), 2.05(t)
4	6.10(t)	3.1	—	0.00(s)[c]	0.95(s), 2.17(s)
5	6.10(d)[d]	—	17.0	—	—
6	6.11(dt)	2.1	14.0	2.31(s)	—
7	6.18(t)	2.4	—	—	0.54(m), 1.26(t), 2.04(t)
8	6.17(t)	2.7	—	0.06(s)[c]	0.99(s), 2.27(s)

a) Measured in deoxygenated CD_2Cl_2 using tetramethylsilane as the internal standard. b) Abbreviations used: s=singlet, d=doublet, t=triplet, dt=double triplet, m=multiplet. c) Chemical shifts were referenced to dichloromethane, whose resonance was δ 5.31 ppm downfield from tetramethylsilane. d) The coupling with ^{31}P could not be detected. See the text.

extension of the π-conjugation, owing to the complex formation.

It has been well known that the aryl 2-chlorovinyl ketones used in this study have a *trans* configuration about the double bond.[7] The ^{1}H-NMR couplings J_{ab} of the vinyl protons, H_a and H_b in **1**, **2**, **5**, and **6**, were about 14.0—18.0 Hz, which were of the order expected for *trans*-AB coupling across a double bond, and indicated that the *trans* arrangement of these protons was retained in these four complexes. No signal for H_a protons could be distinguished owing to the overlapping with many aromatic protons.

H_b resonances of the complexes with the linear and cyclic β-carbonylvinyl groups showed a double triplet and a triplet, respectively. These triplet splittings for both kinds of complexes were ascribed to the coupling with two equivalent phosphorus-31 atoms and indicated a *trans* geometry of the two triphenylphosphine ligands. (In the complex **5**, the coupling with phosphorus-31 could not be detected, because of its fairly fast decomposition.) Table 2 also shows reasonable ν(Pd–Cl) frequencies for the *trans* position to the palladium-carbon σ bond.

In addition, the resonances of the methyl groups in **4** and **8** showed large high-field shifts. The reason for these shifts was probably explained by the ring current of phenyl groups of triphenylphosphine.

The palladium-carbon σ bonds in the eight complexes studied here were stabilized by β-carbonylvinyl groups to some degree, and these complexes were stable in the solid state under dinitrogen at room temperature for several weeks. In a deoxygenated dichloromethane solution, the complexes with the cyclic β-carbonylvinyl groups were stable for more than a week at room temperature, whereas the complexes with the linear ones began to decompose in 1 h. This high stability of the former complexes can be accounted for probably by the steric hindrance of the cyclic β-carbonylvinyl groups against the species which attack the palladium-carbon σ bond.

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