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ORGANOPALLADIUM COMPLEXES DERIVED FROM CHLORO[2-(α-PICOLYLIMINO)-4-PENTANONATO]PALLADIUM(II) AND CARBANIONS FORMED FROM ACTIVE METHYLENE COMPOUNDS

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Summary

A new complex, chloro[2-(α-picolylimino)-4-pentanonato]palladium(II) was prepared, and treated with some carbanions formed from active methylene compounds. Nucleophilic displacement reactions at chlorine afforded new stable complexes containing a palladium—carbon σ-bond in the case of dimethyl malonate, alkyl cyanoacetates, and malononitrile. These complexes were characterized by their IR spectra, ^{1}H and ^{13}C NMR spectra, and electric conductivities.

Introduction

Considerable attention has been devoted to stable palladium—carbon σ-bonds which are stabilized by electron-withdrawing groups attached to the carbon atom and, in many cases, by other ligands coordinated to the palladium atom. It has been reported that these palladium(II) carbon σ-bonds are produced by reactions between halopalladium(II) complexes and a carbanion derived from malononitrile [1,2] or thallium(I) acetylacetonate [3], or between Lewis bases and bis(β-ketoenolato)palladium(II) [3—5] or di-μ-chloro-bis(2-4-η^3-ethyl-3-hydroxy-3-butenoato)dipalladium(II) [6], or by an oxidative addition reaction between tetrakis(triphenylphosphine)palladium(0) and chloroacetonitrile [7].

A Schiff base, 2-(α picolylimino)-4-pentanone (Hpip) prepared from α-picolylamine and acetylacetone, has served as a univalent NNO-type tridentate ligand to form nickel(II) and copper(II) complexes [8]. We expected this ligand to coordinate strongly to palladium and to stabilize the resulting palladium—carbon σ-bond.

This paper deals with some organopalladium(II) complexes obtained by

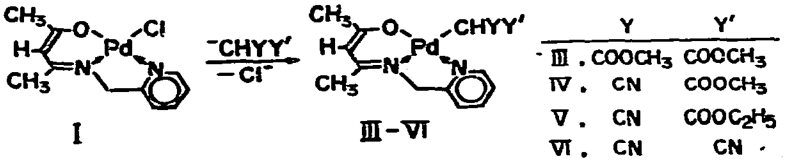

Fig. 1. The reactions of complex I.

nucleophilic displacement reactions of carbanions formed from active methylene compounds with chloro[2-(α-picolylimino)-4-pentanonato]palladium(II) (I).

Experimental

General procedures. Melting points were taken in capillary tubes on a Yanagimoto MP-S3 microstage apparatus and are uncorrected. IR spectra were recorded on a Hitachi model 285 spectrometer. ^{1}H and ^{13}C NMR spectra were run on a JEOL model JNM-MH-100 and FX-100 spectrometers, respectively, using tetramethylsilane as the internal standard. Molar conductivities were measured with a Toa Denpa CM-6A instrument. Solvents were dried and distilled by the usual methods. All preparative operations were performed in an atmosphere of dry nitrogen. α-Picolylamine [9] and Hpip [8] were prepared by literature methods.

Preparation of [PdCl(pip)]. An ethanol solution of Na$_2$[PdCl$_4$] was added dropwise to two molar equivalents of Hpip in ethanol, and the mixture was stirred at room temperature overnight. The resulting precipitate was separated and washed with water, methanol, and diethyl ether to give a pale yellow powder of [PdCl(pip)] (I) in 75% yield.

Halogen metathesis of I. An acetone suspension of I (0.9 mmol) and lithium bromide (2.7 mmol) was heated at reflux for 11 h. The resulting solids were collected, washed successively with water, methanol, and diethyl ether, and dried in vacuo to afford [PdBr(pip)] (II).

Reactions of I with carbanions formed from active methylene compounds. Sodium methoxide (1.26 mmol) in methanol was added to a THF suspension (20 ml) containing I (0.9 mmol) and dimethyl malonate (3.6 mmol). The pale yellow mixture was stirred at room temperature for 24 h. After the solvents were removed, the residue was recrystallized from dichloromethane and diethyl ether to give [Pd(pip){CH(CO$_2$CH$_3$)$_2$}] (III).

Complex I reacted similarly with methyl and ethyl cyanoacetates and molononitrile to yield [Pd(pip){CHCN(CO$_2$CH$_3$)}] (IV), [Pd(pip)-{CHCN(CO$_2$C$_2$H$_5$)}] (V), and [Pd(pip){CH(CN)$_2$}] (VI), respectively.

Results and discussion

The tridentate ligand, Hpip was obtained as yellow oil at ambient temperature [8], and characterized by its IR and ^{1}H NMR spectra. The IR spectrum in a neat state showed the skeletal stretching frequency of the pyridine ring at 1608 cm^{-1}, and two stretching vibrations at 1509 and 1570 cm^{-1} which are assignable to a 2-imino-4-pentanonato group. The ^{1}H NMR spectrum of Hpip in $CDCl_3$ showed three singlets at δ 1.98 ppm (3H, Me), 2.09 ppm (3H, Me), and 5.22 ppm (1H, —CH=) and one doublet at δ 4.73 ppm (2H, N—CH$_2$—, ^3J(HH) 6 Hz). This doublet turned into a singlet with addition of deuterium oxide, and was ascribed to coupling to the proton on the 2-nitrogen atom.

Yields, analytical data, and a few physical properties of complexes I—VI are summarized in Table 1. All these complexes are air-stable in the solid state. Complexes III—VI are soluble in dichloromethane and chloroform, whereas I and II are virtually insoluble in common organic solvents. The IR spectra of I and II in KBr disc showed very similar patterns to Hpip, revealing the retention of the tridentate pip ligand. Moreover, III—VI were also found to retain the pip ligand on the basis of IR spectra and ^{1}H and ^{13}C NMR spectra (Table 2). They exhibited a low conductivity in acetone indicating non-ionic character (Table 1).

The ^{1}H NMR spectrum of III (Table 2) showed a singlet at δ 3.67 ppm of appropriate intensity for two ester methyl groups, which implies their spectroscopic equivalence. Accordingly, there are a few stereochemically possible configurations, as shown in Fig. 2.

A strong ν(C=O) band in the IR spectrum of III (in $CHCl_3$) was observed at 1714 cm^{-1}. This is indicative of the retention of the ester carbonyl groups without bonding of oxygen atom to hydrogen or palladium in an enol fashion. In the ^{1}H NMR spectrum a singlet at δ 3.93 ppm was assignable to a H^a proton of the configuration A, and this chemical shift was very close to those reported for a methine proton attached to palladium in (diacetylmethyl)palladium(II) [3] or in {acetyl(alkoxycarbonyl)methyl}palladium(II) complexes [4,5]. The ^{1}H NMR spectrum exhibited no resonance at lower field than δ 9 ppm, as would have been expected for an enolic H^b proton of configuration B. The H^c proton of configuration C would be reasonably expected to resonate in the range of δ 4.6—5.5 ppm by analogy with those of *O,O'*-chelated β-ketoenolato-

TABLE 1

YIELDS AND PROPERTIES OF THE NEW PALLADIUM(II) COMPLEXES

Complex [a]	Yield [b] (%)	M.p. [d] (°C)	Conductivity [e] Ω^{-1} cm^2 mol^{-1}	Analysis (Found (calcd.) (%))		
				C	H	N
I	75 [c]	245—265	—	39.64 (39.91)	3.84 (3.96)	8.59 (8.46)
II	59	255—265	—	35.34 (35.18)	3.45 (3.49)	7.60 (7.46)
III	31	180—190	0.98	44.79 (45.03)	4.83 (4.72)	6.19 (6.56)
IV	45	143—165	1.71	45.32 (45.76)	4.28 (4.35)	10.47 (10.67)
V	31	144—156	1.18	47.17 (47.13)	4.77 (4.70)	9.95 (10.31)
VI	57	200—213	2.61	46.59 (46.62)	3.79 (3.91)	15.42 (15.53)

[a] All complexes are pale yellow, except VI, which is pale olive. [b] Based on I, except I. [c] Based on $Na_2[PdCl_4]$. [d] With decomposition. [e] Determined for 1.0 × 10^{-3} *M* acetone solution.

TABLE 2

^{1}H- AND ^{1}H-DECOUPLED ^{13}C NMR DATA OF THE PALLADIUM COMPLEXES [a]

Complex	^{1}H NMR data [b]					^{1}H-decoupled ^{13}C NMR data [c]								
	pip [d]			Pd-CHYY′		pip [e]					Pd-CHYY′			
	$\underline{\mathrm{C}}\mathrm{H_3}$	$\mathrm{C}\underline{\mathrm{H}}$	$\mathrm{C}\underline{\mathrm{H_2}}$	$\mathrm{C}\underline{\mathrm{H}}$	Ester alkyl	$\underline{\mathrm{C}}\mathrm{H_3}$	$\underline{\mathrm{C}}\mathrm{H}$	$\underline{\mathrm{C}}\mathrm{H_2}$	$\underline{\mathrm{C}}\mathrm{O}$	$\underline{\mathrm{C}}$=N- or py-2	$\underline{\mathrm{C}}\mathrm{H}$	C=O	C≡N	Ester alkyl
III	2.12 [f]	5.24	5.05	3.93	3.67 ($\mathrm{OC\underline{H}_3}$)	20.6 25.7	98.9	61.1	177.2	162.2, 163.6	28.2	175.4	—	50.8 ($\mathrm{O\underline{C}H_3}$)
IV	1.96 2.01	5.03	4.95	3.29	3.59 ($\mathrm{OC\underline{H}_3}$)	—	—	—	—		—	—	—	—
V	1.99 2.04	5.04	5.00	3.29	4.09 ($\mathrm{OC\underline{H}_2}$) [g] 1.23 ($\mathrm{C\underline{H}_3}$) [h]	20.6 25.3	98.9	61.6	175.9	162.6, 164.1	14.1	174.3	124.9	60.3 ($\mathrm{O\underline{C}H_2}$) 14.4 ($\mathrm{\underline{C}H_3}$)
VI	2.10 2.17	5.32	5.20	3.04	—	—	—	—	—	—	—	—	—	—

[a] δ value (ppm) from TMS. [b] In $\mathrm{CD_2Cl_2}$. Appearing as a singlet, unless noted elsewhere. [c] In $\mathrm{CDCl_3}$. Coupling constants ^1J(CH) are omitted. [d] Pyridine proton resonances are omitted. [e] The other pyridine carbon resonances are omitted. [f] Probably owing to an accidental degeneracy. [g] Quartet [^3J(HH) 7.5 Hz].

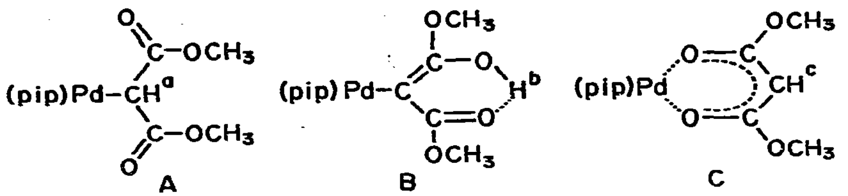

Fig. 2. Possible configurations for III. In configuration B, enol proton would be expected to exchange rapidly between two oxygen atoms.

palladium(II) complexes [3,5], but there was no appropriate resonance assignable to the H^c proton. Moreover, the ^1H-decoupled ^{13}C NMR spectrum of III showed a singlet at δ(C) 28.2 ppm, which was attributed to the palladium-bonded carbon in configuration A. It was not appropriate for the central carbon in the configuration B or C. The chemical shift is reasonable, since the value is fairly close to that (33.5 ppm) of the palladium-bonded carbon in {1,2-bis(diphenylphosphino)ethane}chloro(α-picolyl)paladium(II) [10]. On the basis of these facts and considerations, III was concluded to have configuration A, involving a palladium—carbon σ-bond.

An infrared spectrum of complex IV in chloroform showed a sharp $\nu(C\equiv N)$ band at 2202 cm^{-1}, which is probably a little larger than would be expected for a keteniminato type $[PdN{=}C{=}CH(CO_2CH_3)]$ [1]. A strong $\nu(C{=}O)$ band at 1694 cm^{-1} indicates that the ester group in IV is similar to that of the ester groups in III. The ^1H NMR spectrum of IV in CD_2Cl_2 exhibited a singlet at δ 3.29 ppm ascribable to a methine proton (1H) and a singlet at δ 3.59 ppm for the ester methyl protons (3H), besides the signals of the pip moiety. A ^1H decoupled ^{13}C NMR spectrum of V, an ethyl ester homolog of IV, showed two singlets at δ(C) 14,1 (^1J(CH) 24 Hz) and 124.9 ppm, attributable to the palladium-bonded carbon and a cyano carbon, respectively. It seems unlikely that these two singlets are due to two carbons of the keteniminato type. The data suggest that the palladium atom and the methine carbon in IV and V are σ-bonded.

IR spectrum of VI in chloroform gave two $\nu(C\equiv N)$ bands, a strong band at 2203 cm^{-1} and a weak band at 2155 cm^{-1}. This suggests that VI contains a carbon-bonded dicyanomethyl substituent, $[PdCH(CN)_2]$, rather than the isomeric nitrogen-bonded cyanoketeniminato group, $[PdN{=}C{=}CH(CN)]$, since the latter type would show a strong asymmetric $\nu(N{=}C{=}C)$ band in the range of 2120—2150 cm^{-1} [1] besides the $\nu(C\equiv N)$ band. In the ^1H NMR spectrum in CD_2Cl_2, there was a singlet at δ 3.40 ppm assignable to the methine proton of the dicyanomethyl group, analogously to those of III and IV. Accordingly, VI was assumed to have a palladium-carbon σ-bond similar to those in III, IV, and V.

It is noteworthy that complex I reacted with the carbanions to give the stable organopalladium(II) complexes which contain a palladium—carbon σ-bond, in contrast to the formation of a palladium—nitrogen bond in the case of $[PdCl(CH_2CN)(PPh_3)_2]$ [2] and of $[Pd(CH_3)I(PPh_3)_2]$ [11]. It seems likely that the palladium—carbon σ-bond in III—VI is stabilized both by the electron-withdrawing groups attached to the carbon atom and by the tridentate pip ligand. The organopalladium(II) complexes obtained in the present study are possibly comparable with (acetylacetonato-*O*,*O*′)(diacetylmethyl-*C*) (Lewis base)palladium(II) complexes [3] and with {acetyl(ethoxycarbonyl)methyl} (ethyl acetoacetato-*O*,*O*′) (Lewis base)palladium(II) complexes [5].

Complex I reacted with the carbanions derived from methyl acetoacetate or nitromethane in THF, but pure products could not be isolated. However, I did not react with ethyl nitroacetate or 2-furoyltrifluoroacetone in the presence of an equimolar amount of sodium ethoxide, nor with thallium(I) acetylacetonate in THF.

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