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CATIONIC (CARBENE)ORGANOPALLADIUM(II) COMPLEXES COORDINATED WITH CYCLIC DIOLEFIN OR ORGANIC NITRILE

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Summary

The chloro-bridged (carbene)organopalladium(II) complex, di-μ-chlorobis(1,3-diphenyl-2-imidazolidinylidenato-2-*C*,2′-*C*)dipalladium(II) underwent chlorine abstraction with silver perchlorate in the presence of a cyclic diolefin or an organic nitrile, to give new cationic (carbene)organopalladium(II) complexes coordinated with the respective substrates. These new complexes were characterized by means of elemental analysis, molar conductivities, and IR and ^{1}H NMR spectroscopy.

Introduction

Labile (carbene)(η^2-olefin)metal complexes have been regarded as active species in catalytic olefin metathesis reactions [1,2]. Some stable (carbene)(η^2-olefin)metal complexes have been prepared as model compounds for the active species [3—6]. It has been reported recently that chloro-bridged organopalladium(II) complexes react with an electron-rich olefin, bis(1,3-diphenyl-2-imidazolidinylidene) (L_2) to give neutral (carbene)chloropalladium(II) complexes containing a σ,π-methallyl group or a π-coordinated-chelating alkylpalladium σ-bond [7]. In addition, (carbene)(chloro)organopalladium(II) complexes underwent easily chlorine-abstraction with sodium perchlorate in the presence of Lewis base to afford cationic (carbene)(Lewis base)organopalladium(II) complexes [7,8].

Our interest in the model compounds for olefin metathesis prompted us to investigate reactions of a chloro-bridged (carbene)organopalladium(II) complex, di-μ-chloro-bis(1,3-diphenyl-2-imidazolidinylidenato-2-*C*,2′-*C*)dipalladium(II) [{Pd(dpim)Cl}$_2$] (dpim = 1,3-diphenyl-2-imidazolidinylidenato-2-*C*,2′*C*) (I) [7,9] towards various olefins in the presence of silver perchlorate. In the present paper, we report concerning the resulting new cationic (carbene)-

organopalladium(II) complexes coordinated with cyclic diolefin or organic nitrile.

Experimental

Materials and general procedures

Di-μ-chlorobis(3-t-butylthio-2-methoxy-2-methylpropyl-1-*C*,*S*)dipalladium(II) (II) was prepared by the literature method [10]. Silver perchlorate ($AgClO_4$) and the other reagents were commercial samples and were used without further purification. Solvents were dried by the standard methods and distilled.

Melting points, molar conductivities, and IR and ^1H NMR spectra were measured according to the methods described in a previous paper [8]. Preparative operations were performed under dry nitrogen.

Preparation of the starting complex, I

A *m*-xylene suspension (50 ml) containing II (2.48 mmol) and L_2 (2.70 mmol) was heated at reflux for 40 min. The resulting solid was washed with dichloromethane and diethyl ether and then was treated with silver acetate (4.97 mmol) in refluxing acetone (35 ml) for 1 h. After filtration, a methanol solution (15 ml) of lithium chloride (24.8 mmol) was added to the filtrate. The mixture was stirred at room temperature for 30 min. The resulting solid was collected and washed with methanol and diethyl ether to give I in 59% yield.

Reactions of I with cyclic diolefins in the presence of $AgClO_4$

A benzene solution (25 ml) of $AgClO_4$ (0.28 mmol) was added to a dichloromethane suspension (5 ml) of I (0.14 mmol) and an excess of norbornadiene (nor) (2.7 mmol). The mixture was stirred at room temperature for 2 h and then was filtered. After the filtrate had been evaporated to dryness, the residue was recrystallized from dichloromethane and hexane to yield a yellow powder, $[Pd(dpim)(nor)]ClO_4$ (III).

Similarly, complex I reacted with 1,5-cyclooctadiene (cod) and with dicyclopentadiene (dcp) in the presence of $AgClO_4$ to afford yellow crystals of $[Pd(dpim)(cod)]ClO_4$ (IV) and yellow needles, $[Pd(dpim)(dcp)]ClO_4$ (V), respectively.

Reaction of I with acrylonitrile in the presence of $AgClO_4$

A benzene suspension (2.5 ml) containing I (0.14 mmol), acrylonitrile (5.5 mmol), and $AgClO_4$ (0.28 mmol) was stirred at room temperature for 1 h. After filtration, the resulting solution was evaporated to dryness. The residue was recrystallized from acrylonitrile and diethyl ether to give pale yellow needles $[Pd(dpim)(CH_2{=}CHCN)_2]ClO_4$ (VI).

Reaction of I with acetonitrile and p-tolunitrile

An acetonitrile-benzene (1 : 10) solution (27.5 ml) containing I (0.14 mmol) and $AgClO_4$ (0.28 mmol) was stirred at room temperature for 30 min and filtered. The filtrate was concentrated to about 3 ml and diluted with diethyl ether (25 ml) to yield a pale yellow precipitate. The precipitate was collected and washed with diethyl ether to afford pale yellow crystals [Pd(dpim)-$(CH_3CN)_2]ClO_4$ (VII).

An off-white *p*-tolunitrile complex, [Pd(dpim)$(toln)_2]ClO_4$ (toln = *p*-tolunitrile) (VIII) was prepared using a procedure similar to that used in the preparation of VI. The product was purified by recrystallization from dichloromethane-diethyl ether rather than from acrylonitrile-diethyl ether.

Results and discussion

Preparations of the cationic (carbene)organopalladium(II) complexes

In the previous papers [7,9], the starting complex, I was prepared by the reaction between the sulfur-chelated organopalladium(II) complex, II and L_2 in refluxing *m*-xylene, followed by extraction with hot acetonitrile. However, the extraction took a long time and the overall yield of I was only 47% owing to its poor solubility. Our improved method involves both the conversion of I into a more soluble acetato-bridged dinuclear complex, $[\{Pd(dpim)(OAc)\}_2]$ accompanied by extraction with acetone, and the reconversion of the acetato-bridged complex into I [7,9], and gave a better yield than was obtained in the previous method.

The chloro-bridged dinuclear cyclopalladated carbene complex, I underwent facile chlorine abstraction with $AgClO_4$ in the presence of cyclic diolefins and organic nitriles, to afford mononuclear cationic (carbene)organopalladium(II) complexes, [Pd(dpim)(cyclic diolefin)]ClO_4 (III—V) and [Pd(dpim)(organic nitrile)$_2]ClO_4$ (VI—VIII), respectively (Scheme 1). The yields, elemental analyses, and some physical properties of these complexes are summarized in Ta-

SCHEME 1

i) Cyclic diolefin + $AgClO_4$. ii) Organic nitrile + $AgClO_4$.

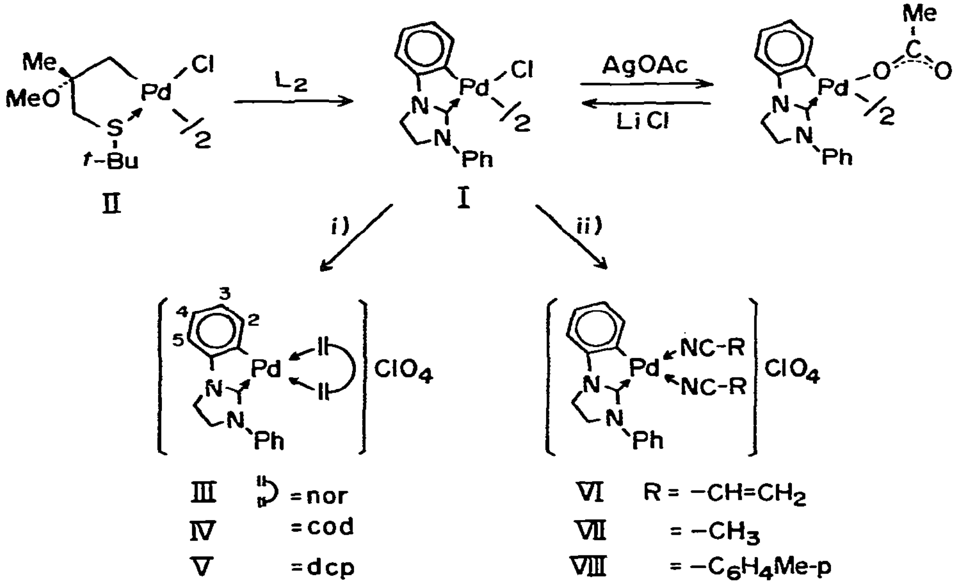

TABLE 1

YIELDS AND ANALYTICAL DATA

Complex		Yield (%)	M.p. [a] (°C)	Analysis: Found (calcd) (%)		
				C	H	N
$[Pd(dpim)(nor)]ClO_4$	III	45	200—220	51.09 (50.89)	4.19 (4.08)	5.27 ((5.39)
$[Pd(dpim)(cod)]ClO_4$	IV	59	146—172	51.52 (51.61)	4.69 (4.71)	5.19 (5.23)
$[Pd(dpim)(dcp)]ClO_4$	V	58	177—189	52.93 (53.68)	4.43 (4.51)	5.05 (5.01)
$[Pd(dpim)(CH_2{=}CHCN)_2]ClO_4$	VI	59	138—149	47.42 (47.30)	3.53 (3.59)	10.34 (10.51)
$[Pd(dpim)(CH_3CN)_2]ClO_4$	VII	58	196—211	44.98 (44.81)	3.75 (3.76)	10.92 (11.00)
$[Pd(dpim)(toln)_2]ClO_4$	VIII	22	148—157	56.39 (56.29)	4.23 (4.11)	8.54 (8.47)

[a] All melting points are uncorrected. With decomposition.

ble 1. It was proposed tentatively that the chlorine-abstraction from I with $AgClO_4$ yielded the intermediate, which had a binuclear structure, containing weak and labile perchlorato—palladium bridges [11], and that the intermediate immediately reacted with substrates present in the reaction system to give the cationic (carbene)organopalladium(II) complexes coordinated with the substrates, III—VIII.

General Properties

Complexes III—VIII are soluble in dichloromethane and acetonitrile, but sparingly soluble in chloroform or benzene, and are quite stable both in the solid state and in dichloromethane. It is worth noting that the σ-aryl— and the carbene—palladium bonds in III—VIII are unreactive toward the coordinated olefin or organic nitrile. The inertness of the σ-aryl—palladium bond is probably due to the chelate effect of the dpim moiety [7—9]. and the lack of reactivity of the coordinated-carbene—palladium bond probably is associated with the electron-donating effect of the two nitrogen atoms adjacent to the carbene carbon [7]. Complexes III—V have three kinds of the carbon—palladium bonds, viz. the σ-aryl—, the carbene—, and the π-coordinated olefin—palladium bonds. They may be regarded as stable model complexes for the catalytic olefin metathesis reactions [1,2,7].

Molar conductivities

Complexes IV, VI, and VII showed a moderate molar conductivity in 1.0 mmol dm^{-3} dichloromethane solution, indicating that each complex exists in an equilibrium between an ionic species and ion-pairs. III—VIII each exhibited a high molar conductivity in acetonitrile, implying the dissociation into two ionic species (see the section concerning ^1H NMR spectra).

TABLE 2

MOLAR CONDUCTIVITIES AND SELECTED IR DATA

Complex	Conductivity [a] $\Lambda(\Omega^{-1}\ \mathrm{cm}^2\ \mathrm{mol}^{-1})$		IR data [b] (cm^{-1})			
	In CH_2Cl_2	In MeCN	ν(Cl—O)	$\nu(C_\phi$—N) [c]	ν{C(carb)—N}	ν(C≡N)
III	—	126	1082	1277	1480	—
IV	50.5	132	1098	1280	1500	—
V	—	122	1098	1281	1496	—
VI	25.0	129	1095	1280	1500	2270
VII	26.9	128	1099	1282	1517	2292 2312
VIII	—	136	1095	1278	1497	2230 2255

[a] In 1.0 mmol dm^{-3}. [b] In KBr disk. [c] ν{C(aromatic)—N}.

IR spectra

III—VIII each showed a strong band near 1280 cm^{-1}, characteristic of ν{(aromatic)—N}, and a medium band at about 1490 cm^{-1}, ascribable to ν{(carbene)—N}, indicating that III—VIII retained the dpim moiety unchanged (Table 2). Furthermore, III—VIII each showed a strong band near 1095 cm^{-1} for the free perchlorate anion.

Complexes VI—VIII showed one or two medium bands in the range 2230—2312 cm^{-1} for ν(C≡N) frequencies. These bands, except the band at 2230 cm^{-1}, shifted about 12—30 cm^{-1} towards higher wave number from the respective values of the free nitriles. The shifts towards higher wave number of the ν(C≡N) bands are associated with the coordination of the nitrile groups to the central metal. Accordingly, acrylonitrile ligands in VI were also σ-coordinated to the palladium atom via the nitrile groups rather than π-coordinated with the olefinic bond.

^1H NMR spectra

The ^{1}H NMR spectra of IV and VI—VIII in CD_2Cl_2 showed both a clearly distinguishable ABCD pattern (4H, ^3J = ca. 7 Hz, ^4J = 1—1.5 Hz) in the range of δ 6.4—7.8 ppm, characteristic of the cyclopalladated phenylene group, and a typical AA′BB′ pattern near δ 4.0 and 4.2 ppm, assignable to the ethylene protons (4H) of the dpim moiety, in addition to a virtual singlet near δ 7.5 ppm (5H) for the unmetallated phenyl group (Table 3). Complex V exhibited the ABCD pattern (4H, phenylene protons) in the range of δ 6.6—7.3 ppm, complicated signals near δ 4.2 ppm (4H, the ethylene protons), and a virtual singlet at δ 7.48 ppm (5H, the unmetallated phenyl protons), whereas III gave complicated signals in the regions of δ 6.5—7.8 (9H, the phenylene and the phenyl protons) and 3.8—4.6 ppm (4H, the ethylene protons). These facts confirm that III—VIII retain the dpim moiety unchanged.

Moreover, IV showed an olefinic resonances at δ 6.29 ppm (4H), and complicated signals near δ 2.44 (4H) and 2.58 ppm (4H), both assignable to the ethylene protons of the coordinated cod ligand. Complex V exhibited three olefinic resonances at δ 4.12 (2H), 5.56 (1H), and 5.66 ppm (1H), an AB type

TABLE 3

THE ^{1}H NMR DATA OF THE CATIONIC CARBENEPALLADIUM(II) COMPLEXES [a]

Complex	dpim moiety					Other ligand [c]	
	Cyclopalladated phenylene group [b]			Phenyl (C_6H_5)	Ethylene NCH_2CH_2N	Olefinic proton $CH{=}CH$ or $CH{=}CH_2$	Others [d]
	3′ or 6′	4′ and 5′	6′ or 3′				
III [e]		6.5–7.8(c) [h]		6.5–7.8 [h]	3.8–4.6(c)	5.96(b, 2H) 6.56(b, 2H)	0.8–2.3(c, 4H, CH_2, CH)
IV	6.67(dd)	6.84(dt), 7.19(dt)	7.37(dd)	7.55(s)	4.20, 4.30(m)	6.29(b, 4H)	2.44(m, 4H, CH_2), 2.58(m, 4H, CH_2)
V	6.62(dd)	6.82(dt), 7.10(dt)	7.28(dd)	7.48(s)	4.2(c)	4.12(b, 2H) 5.56(b, 1H) 5.66(b, 1H)	1.89(q, 2H, 8–CH_2) [f], 2.2(b, 2H) 2.8(b, 1H), 3.0(b, 1H), 3.5(b, 2H)
VI	6.55(dd)	6.77(dt), 7.09(dt)	7.28(dd)	7.41(s)	4.05, 4.21(m)	5.4–6.4(c, 6H) [g]	—
VII [e]	6.53(d)	6.73(t), 7.18(t)	7.41(d) [h]	7.46(s) [h]	4.11, 4.24(m)	—	2.08(bs, 6H, Me)
VIII	6.59(dd)	6.80(dt), 7.13(dt)	7.76(dd)	7.35(s) [h]	4.05, 4.32(m)	—	2.42(s, 6H, Me), 7.1–7.6(m, 8H, C_6H_4) [h]

[a] δ value from TMS, in CD_2Cl_2. Abbreviations used: b = broad, bs = broad singlet, c = complicated, d = doublet, dd = double doublet, dt = double triplet, m = an AA′BB′ type mutliplet, q = an AB type quartet, s = singlet. [b] Coupling constants; ^3J(HH) = *ca.* 7 Hz, ^4J(HH) = 1.0–1.5 Hz. [c] Proton number is given in parentheses. [d] The assignment is given in the parentheses. [e] ^4J(HH)'s of the phenylene group are not distinguished. [f] $\Delta\delta$ = 0.31 ppm, ^2J(HH) = *ca.* 8 Hz. [g] Two ABC type multiplets. [h] Overlapping with the other signals.

quartet at δ 1.89 ppm (2H, $\Delta\delta$ = 0.31 ppm, ${}^2J$ = ca. 8 Hz), and four broad signals (total = 6H) for the remaining protons of the coordinated dcp ligand. Complex VI showed complicated ABC type resonances (6H) in the range of δ 5.4—6.4 ppm for the vinyl protons of the two coordinated acrylonitrile ligands. The ^{1}H NMR spectrum of VIII showed a singlet at δ 2.42 ppm (6H, Me) and two overlapping AA'BB' patterns, due to the *o*- and *m*-protons of the coordinated *p*-tolunitrile ligands.

In the ^{1}H NMR spectrum of VII, the methyl proton resonance appeared as a broad singlet at δ 2.08 ppm at 21°C, indicating that the two coordinated acetonitrile ligands exchange with each other at a considerably fast rate on the NMR time scale. The signal broadened gradually on cooling and separated into two singlets at δ 1.73 and 2.43 ppm at —41°C. This implies that the exchanging motion of the two acetonitrile ligands is quenched at this temperature. The coalescence temperature for the exchange was 13°C. The ^{1}H NMR spectrum of VII in CD_3CN showed a sharp singlet at δ 1.94 ppm and lacked the broad one at δ 2.08 ppm, indicating a fast exchange between the coordinated acetonitrile ligands and the solvent molecules. In the ^{1}H NMR spectrum of VIII in CD_3CN, the *o*- and *m*-protons of the *p*-tolunitrile molecules resonated as an AB type quartet at δ 7.45 ppm (8H, $\Delta\delta$ = 0.24 ppm, ${}^3J$ = 8.3 Hz), and the *p*-methyl protons did as a singlet at δ 2.39 ppm (6H). The data indicate that the *p*-tolunitrile molecules in VIII are replaced by the solvent molecules, acetonitrile. Similarly, IV in CD_3CN exhibited two sharp singlets at δ 2.32 (8H, CH_2) and 5.53 (4H, $CH{=}CH$), implying the replacement of the coordinated cod ligand by the solvent molecules. This is the case with III, V, or VI. These data shows that Pd—olefin and the Pd—nitrile bonds are labile and that the Pd—olefin bonds are not much stronger than the Pd—nitrile bonds.

Reactions with other olefins

Complex I reacted with $AgClO_4$ in the presence of isoprene to give a small amount of a yellow powder. The yellow powder showed two bands at 1280 and 1490 cm^{-1}, characteristic of the carbene ligand, but could not be fully characterized owing to the low yield. When complex I was treated with both $AgClO_4$ and *N*,*N*-dimethylallylamine, a black precipitate was formed, which could not be characterized.

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