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Reactions of Halogeno-bridged Organopalladium(II) Complexes with an Electron-rich Olefin. New Cyclopalladated Carbene Complexes, and (Carbene)chloropalladium(II) Complexes Containing a σ,π-Methallyl Group or a π-Coordinated-chelating Alkyl-Palladium σ-Bond

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A chloro-bridged organopalladium(II) complex, di-μ-chloro-bis(3-*t*-butylthio-2-methoxy-2-methylpropyl-1-*C*,*S*)dipalladium(II) reacted with an electron-rich olefin, bis(1,3-diphenyl-2-imidazolidinylidene) (L_2) to yield a new dinuclear carbene complex, di-μ-chloro-bis(1,3-diphenyl-2-imidazolidinylidenato-2-*C*,2′-*C*)dipalladium(II) (**4**). Complex **4** was treated with thallium acetylacetonate, triisopropyl phosphite, 4-picoline, silver acetate, and L_2, affording the corresponding new carbene complexes. On the basis of spectroscopic properties, these complexes were ascribed to new complexes containing cyclopalladated chelate structure in the carbene ligand. Di-μ-chloro-bis(1-3-η^3-methallyl)dipalladium(II) and di-μ-chloro-bis(6-*exo*-methoxy-3a,4,7,7a-tetrahydro-*endo*-4,7-methanoindene-*endo*-5σ, 2π)dipalladium(II) reacted with L_2 to give new mononuclear (carbene)chloropalladium(II) complexes possessing a σ,π-methallyl group and a π-coordinated-chelating alkyl-palladium σ-bond, respectively.

Recently, some aryl(carbene)palladium(II) complexes were prepared from reactions of chloro-bridged cyclopalladated complexes towards an electron-rich olefin, bis(1,3-diphenyl-2-imidazolidinylidene) $[=\overline{\mathrm{CN(Ph)\text{-}CH_2CH_2N}}\mathrm{(Ph)}]_2$ (L_2).[1] However, few works have been reported as regards isolation and characterization of alkyl- and vinyl(carbene)palladium(II) complexes,[2] while several alkyl-,[3–6] aryl-,[7] and ethynyl(carbene)platinum[8] complexes have been reported.

It is interesting to compare the reactivities of chloro-bridged alkyl-, π-allyl-, and 1-alkenylpalladium(II) complexes towards L_2 with that of the cyclopalladated complexes. The present paper deals with the reactions of the chloro-bridged alkyl- or π-methallylpalladium(II) complexes towards L_2, and with the resulting new types of (carbene)organopalladium(II) complexes, *i.e.* cyclopalladated carbene complexes, and (carbene)chloropalladium(II) ones containing a σ,π-methallyl group or a π-coordinated-chelating alkyl-palladium σ-bond. A preliminary communication of this work has been published recently.[9]

Experimental

General Procedures. Melting points, molecular weight, molar conductivity, and IR and ^{1}H-NMR spectra were determined according to the previous paper.[1] ^{13}C-NMR spectra were measured on a JEOL model FT-100 spectrometer, using tetramethylsilane as an internal standard.

The electron-rich olefin L_2,[10] thallium(I) acetylacetonate,[11] and the chloro-bridged organopalladium(II) complexes, di-μ-chloro-bis(3-*t*-butylthio-2-methoxy-2-methylpropyl-1-*C*,*S*)dipalladium(II) (**1**),[12] di-μ-chloro-bis(1-3-η^3-methallyl)dipalladium(II) (**2**),[13] and di-μ-chloro-bis(6-*exo*-methoxy-3a,4,7,7a-tetrahydro-*endo*-4,7-methanoindene-*endo*-5σ,2π)dipalladium(II) [{Pd(6-MeO-themi)Cl}$_2$] (themi=3a,4,7,7a-tetrahydro-*endo*-4,7-methanoindene-*endo*-5σ,2π) (**3**)[14] were prepared according to the respective literature.

Reaction of 1 with L_2. A mixture of **1** (1.42 mmol) and L_2 (1.44 mmol) in 27.5 ml of *m*-xylene was heated under reflux for 40 min. Resulting black precipitates were collected and extracted with boiling acetonitrile for 10 h. The extracted solid was washed with dichloromethane to afford microcrystals, 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*) (**4**).

Reaction of 4 with Tl(acac). A benzene suspension of **4** (0.11 mmol) and Tl(acac) (0.23 mmol) was heated at reflux for 2 h. After benzene was removed, the residue was extracted with dichloromethane. Addition of diethyl ether to the extract yielded a pale yellow white needle, [Pd(dpim)(acac)] (**5**).

Reaction of 4 with Triisopropyl Phosphite. A tetrahydrofuran (THF) suspension of **4** (0.14 mmol) and triisopropyl phosphite (1.74 mmol) was heated at reflux for 30 min to yield a brown solution. The solution was concentrated at reduced pressure and diluted with hexane to afford a pale yellow solid. The solid was recrystallized from dichloromethane–hexane to give a pale yellow needle, [Pd(dpim)Cl{P(OCHMe$_2$)$_3$}] (**6**).

Reaction of 4 with 4-Picoline. A THF suspension (10 ml) of **4** (0.18 mmol) and 4-picoline (pic) (0.37 mmol) was heated under reflux for 2.5 h. After the solvent was evaporated at reduced pressure, the residue was extracted with dichloromethane. Addition of diethyl ether to the extract gave a pale yellow-white needle, [Pd(dpim)Cl(pic)] (**7**).

Halogen metathesis of **7** with lithium bromide took place in acetone at room temperature, followed by the similar procedures to the preparation of **7**, to afford [PdBr(dpim)(pic)] (**8**).

Reaction of 4 with Silver Acetate. An acetone suspension (12.5 ml) containing **4** (0.14 mmol) and silver acetate (0.30 mmol) was heated at reflux for 2 h. The solvent was removed, and the resulting residue was recrystallized from dichloromethane and hexane to yield an acetato-bridged complex, [{Pd(dpim)(O$_2$CMe)}$_2$] (**9**).

A methanol suspension (10 ml) involving **9** (0.10 mmol) and lithium bromide (0.70 mmol) was heated under reflux for 6 h, and then stirred at room temperature for 1 d. The resulting solids were collected and washed with methanol and diethyl ether to give a bromo-bridged complex, [{PdBr(dpim)}$_2$] (**10**).

Reactions of 4 and 10 with L_2. A *m*-xylene suspension (15 ml) containing **4** (0.28 mmol) and L_2 (0.34 mmol) was refluxed for 2 h. After the solvent was removed with a rotary evaporator, the residue was recrystallized from dichloromethane–hexane to afford a dicarbene complex, [Pd(dpim)ClL]·1/2CH$_2$Cl$_2$ (**11**).

An acetone suspension (12.5 ml) involving **11** (0.19 mmol),

Table 1. Yields and properties of the carbene complexes

Complex		Yield a) %	Mp b) °C	Color	C% Found	C% Calcd	H% Found	H% Calcd	N% Found	N% Calcd
$[\{Pd(dpim)Cl\}_2]$	**4**	46.2 c)	>300	Pale yellow	49.61	49.61	3.58	3.61	7.79	7.71
$[Pd(dpim)(acac)]$	**5**	64.1	225	Off white	56.12	56.29	4.74	4.72	6.58	6.56
$[Pd(dpim)Cl\{P(OCHMe_2)_3\}]$	**6**	76.3	180	Yellow	50.48	50.45	6.02	6.00	4.89	4.90
$[Pd(dpim)Cl(pic)]$	**7**	24.5	212	Off white	55.27	55.28	4.41	4.42	9.10	9.21
$[PdBr(dpim)(pic)]$	**8**	54.7 d)	223	Off white	50.15	50.37	3.89	4.03	8.31	8.39
$[\{Pd(dpim)(O_2CMe)\}_2]$	**9**	75.1	189—202	Yellow	53.39	52.80	4.29	4.17	7.05	7.24
$[\{PdBr(dpim)\}_2]$	**10**	100 e)	246—254	Pale yellow	43.93	44.20	3.02	3.22	6.69	6.87
$[Pd(dpim)ClL]\cdot\frac{1}{2}CH_2Cl_2$	**11**	70.9	240—260	White	58.24	58.34	4.61	4.50	8.80	8.92
$[Pd(dpim)L(pic)]ClO_4$	**12**	56.4 f)	158—168	Pale yellow	57.88	58.23	4.66	4.62	9.31	9.31
$[PdBr(dpim)L]$	**13**	25.9 g)	220—260	Pale yellow	56.64	57.21	4.36	4.32	8.65	8.89
$[Pd(\sigma,\pi\text{-}CH_2CMe{=}CH_2)ClL]$	**14**	65.8 h)	150—163	Cream	54.62	54.43	5.13	5.05	6.64	6.68
$[Pd(6\text{-}MeO\text{-}themi)ClL]$	**15**	71.3 i)	153—157	Off white	58.57	59.21	5.58	5.54	5.25	5.35

a) Based on **4**, unless noted elsewhere. b) With decomposition. c) Based on **1**. d) Based on **7**. e) Based on **9**. f) Based on **11**. g) Based on **10**. h) Based on **2**. i) Based on **3**.

Table 2. Characteristic IR bands of the carbene complexes

Complex	$\nu(C_{carbene}\text{-}N)$	$\nu(C_{\phi}\text{-}N)$ b)	$\nu(Pd\text{-}Cl)$	Others
4	1480, 1495	1280	239, 258	—
5	1475, 1495	1275	—	$1510+1580\{\nu(C{=}C)+\nu(C{=}O)\}$
6	1485, 1500	1280	280	$1100\{(\nu(C\text{-}O)\}$
7	1480, 1495	1280	305	$1568+1620\{\nu(C{=}N)+\nu(C{=}C)\}$ c)
8	1495	1275	—	$1565+1615\{\nu(C{=}N)+\nu(C{=}C)\}$ c)
9	1480	1275	—	$1405\{\nu_s(OCO)\}$, $1580\{\nu_a(OCO)\}$
10	1485	1280	—	—
11	1465, 1490	1275	246	—
12	1485	1270	—	$1570+1610\{\nu(C{=}N)+\nu(C{=}C)\}$ c) $1100\{\nu(Cl\text{-}O)\}$
13	1485	1270	—	—
14	1485	1270	272	—
15	1485	1275	274	$1075\{\nu(C\text{-}O)\}$

a) In cm^{-1}, in KBr disk. b) $\nu\{C(aromatic)\text{-}N)\}$. c) For the pyridine ring.

4-picoline (0.54 mmol), and sodium perchlorate–water(1/1) $\{Na[ClO_4]\cdot H_2O\}$ (0.21 mmol) was heated under reflux for 1.5 h. After acetone had been evaporated, the resulting residue was recrystallized from acetonitrile-diethyl ether to give an ionic complex, $[Pd(dpim)L(pic)]ClO_4$ (**12**).

Complex **10** (0.10 mmol) reacted with L_2 (0.10 mmol) in refluxing *m*-xylene (10 ml) for 2 h, followed by the similar treatment to **11**, to yield [PdBr(dpim)L] (**13**).

Reaction of 2 with L_2. The electron-rich olefin L_2 (0.27 mmol) was added to a toluene solution (10 ml) of **2** (0.25 mmol). The mixture was heated under reflux for 10 min. Addition of hexane to the resulting solution afforded cream needles, $[Pd(\sigma,\pi\text{-}CH_2CMe{=}CH_2)ClL]$ (**14**).

Reaction of 3 with L_2. A toluene suspension (12.5 ml) containing **3** (0.16 mmol) and L_2 (0.17 mmol) was heated under reflux for 30 min. Addition of petroleum ether to the resulting solution gave an off-white needle, [Pd(6-MeO-themi)ClL] (**15**).

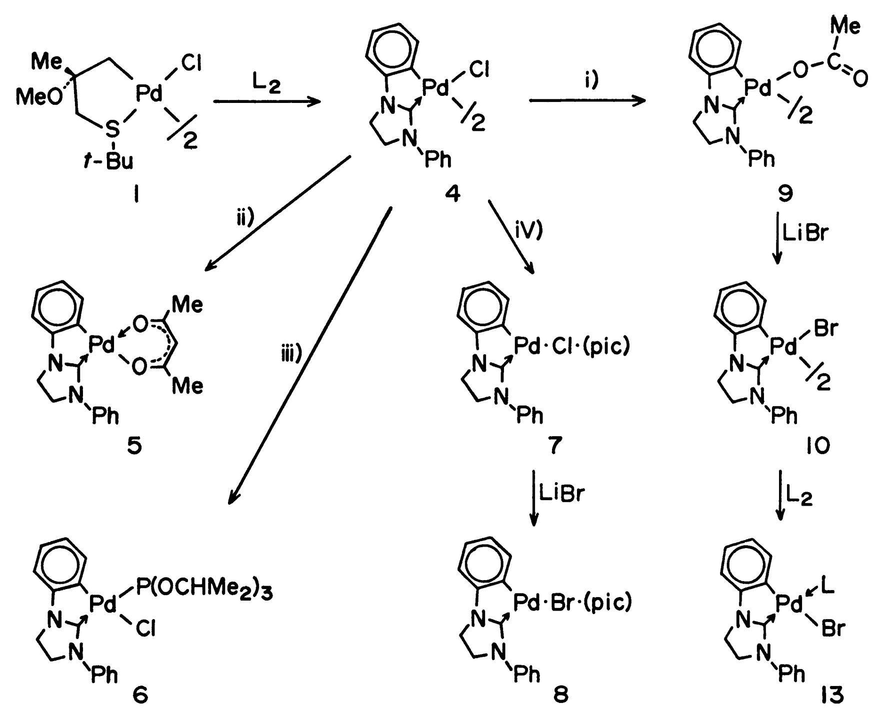
*Reactions of **14** and **15** with L_2.* A benzene-*m*-xylene mixture (1:1, 12 ml) involving **14** (0.25 mmol) and L_2 (0.24 mmol) was heated under reflux for 2.7 h. After the solvents were evaporated at a reduced pressure, the resulting solid was recrystallized from dichloromethane and hexane to give **11** in 23.4% yield.

Similarly, **15** (0.19 mmol) reacted with L_2 (0.20 mmol) in *m*-xylene (10 ml) under reflux for 11 h to afford **11** in 25.2% yield.

Results and Discussion

General Properties. Yields, analytical data, and some physical properties of the new (carbene)palladium(II) complexes are summarized in Table 1. All these complexes are air-stable in the solid state. Mononuclear complexes, **5**—**8** and **12**—**15** are fairly soluble in dichloromethane and chloroform, whereas the halogeno-bridged dinuclear complexes, **4** and **10** are sparingly soluble in usual oragnic solvents. The IR spectra of the twelve complexes showed a strong band near 1280 cm^{-1}, characteristic of $\nu\{C(aromatic)\text{-}N\}$ and a medium band at *ca.* 1490 cm^{-1} for $\nu\{C(carbene)\text{-}N\}$ (Table 2).

*Cyclopalladated Carbene Complexes, **4**—**10**.* The sulfur-chelated alkylpalladium(II) complex, **1** reacted with L_2 in refluxing xylene to afford the cyclopalladated complex, **4**. In the IR spectrum of **4**, two bridging $\nu(Pd\text{-}Cl)$ bands were observed at 258 and 239 cm^{-1}. The chlorobridged complex, **4** reacted with Tl(acac), triisopropyl phosphite, 4-picoline, and silver acetate,



Scheme 1. i) AgO_2CMe; ii) Tl(acac); iii) $P(OCHMe_2)_3$; iv) 4-picoline.

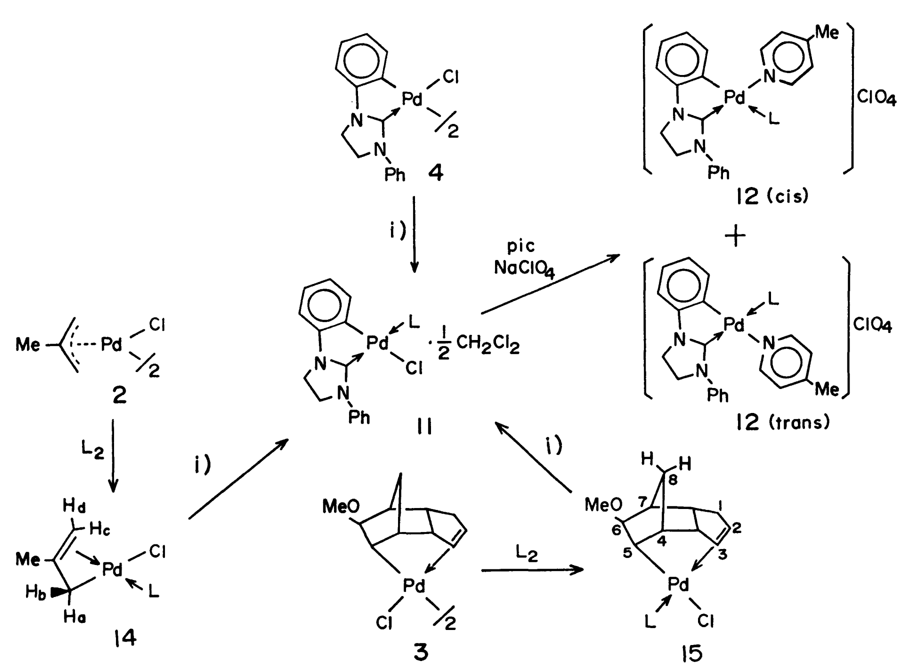
TABLE 3. CHARACTERISTIC ^{1}H-NMR DATA OF THE CARBENE COMPLEXES[a]

Complex	dpim or L $(NC\underline{H}_2C\underline{H}_2N)$	The other groups	
		$C\underline{H}_3$	The other protons[b]
5	3.9—4.5(m)	1.36(s), 1.96(s)	5.20(s, 1H, acac-C$\underline{H}$)
6[c]	3.9—4.5(m)	1.33(d)[d]	5.0(c, 1H, OC$\underline{H}$Me$_2$)[d]
7	3.9—4.5(m)	2.15(s)	6.51(d, 2H, H_β),[d] 8.16(d, 2H, H_α)[d]
8	3.9—4.3(m)	2.17(s)	8.18(d, 2H, H_α)[d,e]
9[c]	3.0—4.0(c)	1.27(s)	—
11[b,f]	3.2—3.45(c, 2H) 3.6—3.95(c, 6H)	—	5.71(s, 1H, ½CH_2Cl_2)
12[b]	3.3—4.0(c, 4H) 4.05(s, 2.8H) 4.36(s, 1.2H)	2.16(s, 0.9H) 2.34(s, 2.1H)	6.23(d, 0.6H, H_β)[d] 6.63(d, 1.4H, H_β)[d] 8.97(d, 2H, H_α)[d]
13[b]	3.2—4.2(c, 4H) 3.92(s, 4H)	—	—
14	4.1—4.5(m)	1.44(s)	1.91(s, 1H, H_a), 2.91(d, 1H, H_b)[g] 2.95(s, 1H, H_c), 3.95(d, 1H, H_d)[g]
15[c]	4.0—4.6(m)	2.64(s)	6.37(s, 2H, C$\underline{H}$=C$\underline{H}$) 0.97(d, 1H, 8-H_a), 1.21(d, 1H, 8-H_b)[h,i]

a) δ value (ppm) from TMS. In CD_2Cl_2, unless noted elsewhere. Abbreviations used; c=complicated, d=doublet, m=an AA′BB′ type multiplet, s=singlet, phenyl and phenylene protons are omitted. b) Approximate proton numbers are given in parentheses. c) In $CDCl_3$. d) $^3J_{HH}$=*ca.* 7 Hz. e) H_β was not distinguished. f) In DMSO-d_6. g) $^4J_{HH}$=2.5 Hz. h) $^2J_{H_aH_b}$=8 Hz. i) 1-Methylene and the other methine resonances are not distinguished.

and resulted in the splitting of the chloro-bridged bonds to yield the corresponding complexes, **5**, **6**, **7**, and **9**, respectively (Scheme 1). Bridging acetato ligands of **9** in Nujol mull showed two bands at 1560 and 1420 cm^{-1}. Complexes **7** and **9** were treated with lithium bromide to give the corresponding bromo complexes, **8** and **10**, respectively.

The $^{13}C\{^1H\}$-NMR spectrum of **5** in CD_2Cl_2 exhibited a resonance at δ 192.1 from TMS, characteristic of the carbene carbon (2-C). Three quarternary carbon resonances at δ 149.2, 139.2, and 140.3 are ascribed to a palladium-bonded carbon (2′-C), an *N*-substituted carbon (1′-C) of an *o*-phenylene group, and an *N*-substituted carbon (1″-C) of the uncoordinated phenyl group, respectively,[15] by comparison with the cases of **6** and its related complexes.[1,16] Two oxygen-bonding carbons of acetylacetonato ligand resonated at δ 187.5 and 186.5, and two methyl carbons did



Scheme 2. i) With L_2 in refluxing *m*-xylene or xylene–benzene mixture, followed by recrystallization from dichloromethane–hexane.

at δ 28.0 and 27.3, indicating the non-equivalence of two coordination sites of the acetylacetonato ligand, due to the cyclopalladation of the carbene ligand. In addition, a mass spectrum of **5** exhibited a parent-ion isotope pattern centered at 426 of *m/e* in accord with the proposed structure. Complex **5** showed C=O and C=C stretching bands characteristic of the enolate chelate.

The $^{13}C\{^1H\}$-NMR spectrum of **6** was observed in $CDCl_3$, and gave a doublet at δ 200.6 (^2J=205.1 Hz), attributable to a carbene carbon. This large coupling constant indicates unambiguously that the triisopropyl phosphite ligand is situated *trans* to the carbene carbon.[16] Two doublets at δ 44.6 [^4J(CP)=3.9 Hz] and 53.8 [^4J(CP)=8.8 Hz] were assigned to two methylene carbons of the 2-imidazolidinylidene ring. Remaining two doublets at δ 121.9 [^4J(CP)=4.9 Hz] and 138.5 [^3J(CP)=10.7 Hz] were tentatively assignable to 6′-C and 1′-C of the cyclopalladated phenylene group, respectively.[17] These splittings of the carbon resonances were attributable to a long range phosphorus-carbon coupling.[16] Two singlets at δ 140.7 and 150.2 were ascribed to the *N*-substituted aromatic carbon (1″-C) of the unmetallated phenyl group and a palladium-bonded carbon (2′-C), respectively.[17] It is worth noting that a palladium-substituted phenylene carbon in the cyclopalladated complexes resonates in the range of δ 146—151.[1,18]

The ^1H-NMR spectra of **5**—**8** showed complicated signals in the range of δ 6.4—8.6, which were attributed to both the cyclopalladated *o*-phenylene group and the unmetallated phenyl one. Moreover, the spectra gave an AA′BB′ type multiplet for the ethylene group of the dpim moiety in the region of δ 3.9 to 4.5 (Table 3). Complex **9** exhibited complicated signals in the range of δ 3.0—4.0, which were assignable to the ethylene protons of the dpim moiety.[19]

On the basis of these facts, **4**—**10** were ascribed to new complexes containing cyclopalladated chelate structure within the carbene ligand. It seems likely that the halogeno-bridge splitting reaction of **1** with L_2 afforded an intermediate of a carbene complex retaining the 3-*t*-butylthio-2-methoxy-2-methylpropyl moiety, and that the moiety then abstracted immediately an *ortho*-proton from a phenyl ring attached to the 2-imidazolidinylidene ligand to be eliminated. The presence of such the intermediate is readily inferred from the isolation of (carbene)(π-coorinated chelating alkyl)palladium(II) complex **15**, as stated later. Similar cyclometallated structures have been reported concerning {(alkylamino)(phenylamino)methylenato-1-*C*,2′-*C*}platinum(IV) complexes,[20] {bis(*p*-tolylamino)-methylenato-1-*C*,2′-*C*}platinum(II) ones,[21] and (1,3-di-*p*-tolyl-2-imidazolidinylidenato-2-*C*,2′-*C*)ruthenium(II) ones.[22]

Di(carbene)palladium(II) Complexes. The halogeno-bridged cyclopalladated complexes, **4** and **10** reacted with L_2 in refluxing xylene to yield the dicarbene complexes, **11** and **13**, respectively. The ^1H-NMR spectrum of **11** in DMSO-d_6 showed a singlet at δ 5.7 (1H, 1/2 CH_2Cl_2, as solvent of crystallization) and complicated signals near δ 3.3 (2H) and 3.8 (6H), which were ascribed to the ethylene protons of the cyclopalladated and unmetallated 1,3-diphenyl-2-imidazolidinylidene groups.

Complex **11** reacted with both 4-picoline and Na[ClO_4]·H_2O in refluxing acetone to afford **12**. Molar conductivity of **12** for 1.0×10^{-3} M acetone solution at 25 °C was 132 Ω^{-1} cm^2/mol, implying a 1:1 electrolyte. Its ^1H-NMR spectrum in CD_2Cl_2 exhibited two 4-picoline-methyl singlets at δ 2.16 (*ca.* 0.9H) and 2.34 (*ca.* 2.1H), and three kinds of the 2-imidazolidinylidene-ethylene protons; one at δ 3.3—4.0 (4H, complicated), the second at δ 4.05 (*ca.* 2.8H, singlet),

TABLE 4. THE REACTIVITIES OF THE CHLORO-BRIDGED DINUCLEAR ORGANOPALLADIUM(II) COMPLEXES WITH L_2

Bond type	Complex	Mp/°C	Reaction temp/°C	Main product
Pd-σ-aryl	$[Pd_2\{C_6H_4\text{-}CMe(N{=}OH)\text{-}1\text{-}C,N\}_2Cl_2]$	>210[29]	139	$[Pd\{C_6H_4\text{-}CMe(N{=}OH)\text{-}1\text{-}C,N\}ClL]$[1]
Pd-σ-aryl	$[Pd_2(C_6H_4\text{-}CH_2NMe_2\text{-}1\text{-}C,N)_2Cl_2]$	185—187[28]	139	$[Pd(C_6H_4\text{-}CH_2NMe_2\text{-}1\text{-}C,N)ClL]$[1]
Pd-σ-aryl	$[Pd_2\{C_6H_4\text{-}CPh(N{=}OH)\text{-}1\text{-}C,N\}_2Cl_2]$	150—152[29]	139	$[Pd\{C_6H_4\text{-}CPh(N{=}OH)\text{-}1\text{-}C,N\}ClL]$[1]
Pd-π-methallyl	$[\{Pd(\eta^3\text{-}CH_2CMe{=}CH_2)Cl\}_2]$ **2**	166—168[13]	110	$[Pd(\sigma,\pi\text{-}CH_2CMe{=}CH_2)ClL]$ **14**
Pd-σ,π-methallyl	$[Pd\text{-}\sigma,\pi\text{-}CH_2CMe{=}CH_2)ClL]$ **14**	150—168	97	[Pd(dpim)ClL] **11**
Pd-σ-alkyl	$[Pd_2\{CH_2CMe(OMe)CH_2S\text{-}{}^tBu\}_2Cl_2]$ **1**	178—184[12]	139	$[\{Pd(dpim)Cl\}_2]$ **4**
Pd-σ-alkyl	$[\{Pd(6\text{-}MeO\text{-}themi)Cl\}_2]$ **3**	166—170[14]	110	[Pd(6-MeO-themi)ClL] **15**
Pd-σ-alkyl	[Pd(6-MeO-themi)ClL] **15**	153—157	139	[Pd(dpim)ClL] **11**
Pd-σ-alkyl	$[\{Pd(8\text{-}MeO\text{-}C_8H_{12}\text{-}1\sigma,\ 4\pi)Cl\}_2]$	130—135[14]	45	"The pale yellow powder"[a]
Pd-σ-alkyl	$[\{Pd(6\text{-}MeO\text{-}C_7H_8\text{-}5\sigma,\ 2\pi)Cl\}_2]$	108—110[30]	80	Pd black and black oil.[a]
Pd-σ-1-alkenyl	$[\{Pd(CH{=}CCl\text{-}CMe_2NMe_2\text{-}1\text{-}C,N)Cl\}_2]$	172—175[31]	139	"The pale olive powder"[a]

a) See the text.

and the third at δ 4.36 (*ca.* 1.2H, singlet) (Table 3). The data indicate unambiguously that **12** involves two kinds of both the picoline-methyl groups and of the unmetallated 2-imidazolidinylidene moieties in the same ratio of about 7:3. On the basis of these facts, the elemental analyses, and the conductivity data, **12** was ascribed to a mixture of *cis* and *trans* isomeric cationic di(carbene)palladium(II) complexes, each of which contains the cyclopalladated and the unmetallated 1,3-diphenyl-2-imidazolidinylidene moieties. The population ratio of the *cis*: *trans* isomers was about 7:3. The ethylene resonances of the dpim moieties in these isomers overlapped with each other. In consideration of the relative electron-deficient effect of the carbene ligand,[16,23] the lower-field methyl resonance at δ 2.34 and the higher-field ethylene singlet at δ 4.05 were assigned to the major *cis* isomer. The two ethylene singlets of the unmetallated 2-imidazolidinylidene moieties were possibly due to an accidental coincidence, since the signals did not changed actually on cooling to -35 °C.

Carbenepalladium(II) Complexes Containing a σ,π-Methallyl Group or a π-Coordinated-chelating Alkyl-palladium σ-Bond. Complex **2** and **3** reacted with L_2 in refluxing toluene to give **14** and **15**, respectively. The ^1H-NMR spectrum of **14** in $CDCl_3$ showed three singlets at δ 1.44 (3H, Me), 1.91 (1H, H_a), and 2.95 (1H, H_c), and two doublets at δ 2.91 [1H, H_b, $^4J(H_bH_d)=2.5$ Hz] and 3.95 (1H, H_d). The doublets of the H_b and H_d were ascribed to a long range coupling through the allylic double bond.[24] This pattern of the methallyl proton resonances indicates that the π-methallyl group in **2** was converted into a σ,π-methallyl one with the displacement of one of the two bridging chlorine atoms by L, similarly to the case of chloro(σ,π-methallyl)(neutral Lewis base)palladium(II).[25] Moreover, **14** exhibited the AA'BB' type resonance for the ethylene protons of L, in the range of δ 4.1 to 4.5.

^1H-NMR spectrum of the 6-MeO-themi moiety in **15** showed a methyl resonance at δ 2.64 (3H, singlet), bridge-head methylene ones at δ 0.97 and 1.21 (2H, an AB type quartet), and olefinic one at δ 6.37 (2H, virtually singlet), besides complicated signals in the region of δ 1.6—3.0. In addition, **15** gave AA'BB' type resonances for the ethylene protons of L near δ 4.3 and aromatic resonances in the range of δ 7.2 to 8.4. On the basis of these data, elemental analyses, and IR spectrum, **15** was assigned to a new carbenepalladium(II) complex, which contains the 6-MeO-themi moiety coordinated to the central metal.

It is significantly noteworthy that **14** and **15** involve three kinds of carbon-palladium bond; the carbene-, the alkyl σ-, and the π-olefin-palladium bonds, and that they are regarded as model compounds of the active species in catalytic olefin metathesis reactions.[26] Only four papers have ever been published as concerns isolation of stable complexes which contain both a carbene- and a π-olefin-metal bonds.[27] Complexes **14** and **15** reacted with L_2 in a more severe condition, namely in refluxing xylene, and afforded the dicarbene complex **11** in about 25% yield after recrystallization from dichloromethane–hexane.

Reactivities of the Chloro-bridged Organopalladium(II) Complexes towards L_2. In conclusion, the reactivities of the σ-aryl-, π-methallyl-, σ,π-methallyl-, σ-alkyl-, and σ-1-alkenylpalladium(II) complexes towards L_2 are summarized in Table 4. The cyclopalladated σ-aryl complexes retained the palladium-aryl σ-bond unchanged during the reaction with L_2.[1] The π-methallyl complex, **2** reacted with L_2 in refluxing toluene to give **14**, retaining the palladium-σ,π-methallyl bond, which was furthermore converted into the palladium-aryl σ-bond of the dpim moiety through the reaction with additional L_2 at 97 °C.

The π-coordinated-chelating σ-alkylpalladium(II) complex, **3** and **15** reacted with L_2 in similar manners to the π-methallyl complex, **2** and to the σ,π-methallyl one, **14**, respectively. However, an analogous complex, di-μ-chloro-bis(8-*exo*-methoxycyclooct-4-enyl-*endo*-1σ,4π)dipalladium(II)[14] was treated with L_2 at 45 °C to afford a small amount of a pale yellow powder, which showed two IR bands assignable to the carbene ligand but could not be characterized in details owing to the low yield. Di-μ-chloro-bis(6-*exo*-methoxybicyclo[2,2,1]hept-2-ene-*endo*-5σ,2π)dipalladium(II), having a relatively low melting point,[30] reacted with L_2 in refluxing benzene for 10 min to yield *ca.* 70%

of palladium black and a small amount of black oil, which was impossible to be characterized. The sulfur-chelated σ-alkylpalladium bond in **1** was converted into the palladium-aryl σ-one of the dpim moiety in the reaction with L_2, not only in refluxing *m*-xylene, but also in refluxing toluene.

A 1-alkenylpalladium(II) complex, di-μ-chloro-bis(2-chloro-3-dimethylamino-3-methyl-1-butenyl-1-*C*,*N*)dipalladium(II)³¹⁾ yield only a small amount of a pale olive powder, which exhibited two bands at 1490 and 1275 cm^{-1}, characteristic of the carbene ligand, but could not be full characterized because of the low yield.

It is noteworthy that the carbene ligands studied in the present paper do not insert into the carbon-palladium σ-bond. The innertness of the carbene ligands is probably due to the electron-donating character of two nitrogen atoms attached to the carbene carbon. This shows sharp contrasts with hexafluoro-3-propylidene which inserts into a hydrido-platinum bond,³²⁾ and with alkyl isocyanide which does into an alkyl-palladium σ-bond.³³⁾

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