BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 51 (9), 2548—2550 (1978)

New Palladium(II) Carbene Complexes Containing a Cyclometallated Aryl Group[†]

Katsuma Hiraki,* Masayoshi Onishi,* Kiyoshi Sewaki, and Keiichi Sugino

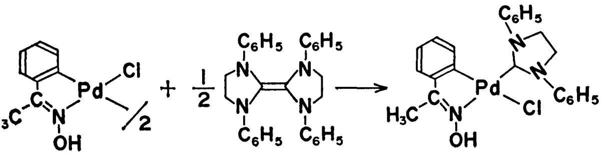
Department of Industrial Chemistry, Faculty of Engineering,
Nagasaki University, Bunkyo-machi, Nagasaki 852

(Received October 11, 1977)

New carbene complexes of (acetophenone oxime, 2-*C*,*N*)chloro(1,3-diphenylimidazolidin-2-ylidene)palladium(II) (**1**), (benzophenone oxime,2-*C*,*N*)chloro(1,3-diphenylimidazolidin-2-ylidene)palladium(II) (**2**), and chloro(*N*,*N*-dimethylbenzylamine,2-*C*,*N*)(1,3-diphenylimidazolidin-2-ylidene)palladium(II) (**3**) have been prepared by reactions between dimeric cyclopalladated complexes and 1,1′,3,3′-tetraphenyl-2,2′-biimidazolidinylidene. Chlorine atoms were shown to be situated at the *trans* position to the aryl-palladium σ bond on the basis of IR spectra. These carbene complexes underwent halogen metathesis with LiBr to yield the corresponding bromo derivatives. Triphenylphosphine displaced the chlorine atom in **1**, **2**, and **3**, converting each to a cationic carbene complex, in which the nitrogen donor of cyclopalladation moiety remained coordinated to palladium.

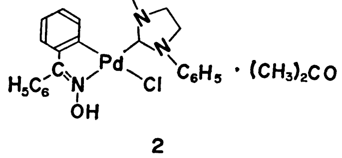
The electron rich olefin, 1,1′,3,3′-tetraphenyl-2,2′-biimidazolidinylidene,[1] has been used as an organic precursor for the syntheses of transition metal carbene complexes by Lappert *et al.*[2] Some palladium(II) carbene complexes have been prepared in reactions between di-μ-chloro-dichlorobis(trialkylphosphine)dipalladium(II) and the electron rich olefin.[2]

We have been interested in the halogen-bridge splitting reaction of cyclopalladated dimeric complexes and presented earlier a brief report on some palladium(II) complexes prepared with this method.[3] This paper will deal with several new palladium(II) complexes, which have been prepared by the halogen-bridge splitting reactions between the cyclopalladated dimeric complexes and the electron rich olefin. The product has been shown to contain both the carbene ligand and an aryl-palladium σ bond.

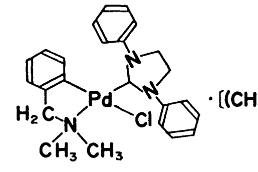


L₂

1



2



3a ; n = 1/2
3b ; n = 0

Experimental

General Procedures. Melting points were determined in capillary tubes on a Yanagimoto MP-S3 microstage apparatus and are uncorrected. IR spectra were recorded on a Hitachi model 285 spectrometer and a Shimadzu IR 450 spectrometer. ^{1}H-NMR spectra were run on a Japan Electron Optics Laboratory model JNM-MH-100 spectrometer (100 MHz), using tetramethylsilane as an internal standard. ^{13}C-NMR spectra were measured on a Bruker WH-90 spectrometer, operating the Fourier transform model at 22.63 MHz.[4] Molecular weights were determined using a JEOL model JMS-01SG double-focussing mass spectrometer referring to parent ion peaks. Molar conductivities were measured with a Toa Denpa CM-6A instrument.

Starting materials, $[\{PdCl(C_6H_4\text{-}C(=N\text{-}OH)R, 2\text{-}C,N)\}_2]$,[5] $[\{PdCl(C_6H_4CH_2NMe_2,2\text{-}C,N)\}_2]$,[6] and 1,1′,3,3′-tetraphenyl-2,2′-biimidazolidinylidene (L_2)[7] were prepared and purified according to the methods described in the literature. Reactions were performed under dry nitrogen.

Reactions of the Electron Rich Olefin with the Dimeric Cyclopalladated Complexes. The olefin L_2 (0.45 g) and $[\{PdCl(C_6H_4\text{-}C(=N\text{-}OH)CH_3,2\text{-}C,N)\}_2]$ (0.56 g) were heated under reflux in *m*-xylene for 10 min. The reaction mixture was allowed to cool and then filtered. The separated solid was recrystallized from dichloromethane and hexane to give a pale yellow crystalline powder, $[PdCl(C_6H_4\text{-}C(=N\text{-}OH)CH_3, 2\text{-}C,N)L]$ (L = 1,3-diphenylimidazolidin-2-ylidene) (**1**), 0.58 g.

$[PdCl(C_6H_4\text{-}C(=N\text{-}OH)C_6H_5,2\text{-}C,N)L]\cdot(CH_3)_2CO$ (**2**) and $[PdCl(C_6H_4CH_2NMe_2,2\text{-}C,N)L]\cdot 1/2(CH_3)_2CO$ (**3a**) were prepared in a similar method as used for **1**, but acetone was used for the recrystallization. Complex **3a** was converted into a non-solvated complex (**3b**) by recrystallization from acetone and diethyl ether. The removal of acetone was confirmed by elemental analysis, IR, and ^{1}H-NMR spectrum of **3b**.

*Halogen Metathesis Reactions of **1**, **2**, and **3a**.* The chloro complex **1** (0.20 g) was treated with an excess of LiBr (0.1 g) in methanol under reflux for 4 h. The suspension was cooled and filtered. The separated solid was washed with methanol and diethyl ether to yield a pale yellow powder, $[PdBr(C_6H_4\text{-}C(=N\text{-}OH)CH_3,2\text{-}C,N)L]$ (**4**), 0.14 g.

The complex **2** (0.15 g) and LiBr (0.05 g) were heated under reflux in acetone for 5 h. The solvent was evaporated, and the residue was washed with methanol and diethyl ether to give $[PdBr(C_6H_4\text{-}C(=N\text{-}OH)C_6H_5,2\text{-}C,N)L]$ (**5**), 0.12 g.

$[PdBr(C_6H_4CH_2NMe_2,2\text{-}C,N)L]$ (**6**) was obtained similarly.

*Reactions of **1**, **2**, and **3a** with Triphenylphosphine.* The complex **1** (0.20 g) and PPh_3 (0.15 g) in acetone were heated

---

[†] A preliminary report of this work was presented at the 36th National Meeting of the Chemical Society of Japan, Higashi-Osaka, April 1977.

TABLE 1. SYNTHESES OF NEW PALLADIUM(II) CARBENE COMPLEXES

	Color	Yield %	Mp[a] °C	Found (Calcd) % C	H	N	Λ_M[b]	M+[c] (Calcd)
1	Pale yellow	57.6	230—268	55.44 (55.44	4.41 4.45	8.30 8.43)	2.15[d]	499 (498.3)
2	Cream	35.2	246—247	60.17 (60.21	4.76 4.89	6.97 6.79)	1.48[d]	560 (560.4)[f]
3a	White	55.8	215—272	58.11 (58.07	5.50 5.54	7.92 7.96)	7.18[d]	498 (498.3)[f]
3b	White		207—294	57.63 (57.85	5.29 5.26	8.52 8.43)		
4	Pale yellow	64.5	241—295	51.33 (50.90	4.07 4.09	7.77 7.74)		
5	Pale yellow	82.8	255—259	55.71 (55.61	4.02 4.00	7.03 6.95)		
6	White	65.8	227—235	53.29 (53.11	4.92 4.83	7.68 7.74)		
7	White	15.2	182—192	59.72 (59.72	4.58 4.52	5.13 5.00)	123[e]	
8	Cream	34.8	176—177	62.10 (62.31	4.43 4.43	4.65 4.74)	136[e]	
9	White	24.9	181—195	61.82 (61.17	5.15 5.01	5.13 5.10)	130[e]	

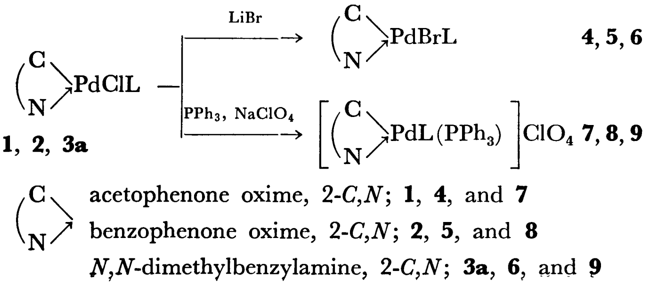
a) With decomposition. b) Molar conductivity, Ω^{-1} cm^2 mol^{-1}, at 25 °C, 10^{-3} mol/l. c) The strongest peak in the parent-ion isotope pattern of mass spectrum. d) In acetonitrile. e) In acetone. f) Calculated value for the non-solvated complex.

for 5 h with stirring. The reaction mixture was allowed to cool and filtered. Sodium perchlorate–water(1/1) (0.06 g) was added to the filtrate. After the suspension was stirred overnight, the solvent was removed *in vacuo*. The residue was recrystallized from dichloromethane and diethyl ether to afford a white crystalline product, $[Pd(C_6H_4\text{-}C(=N\text{-}OH)CH_3, 2\text{-}C,N)L(PPh_3)]ClO_4$ (**7**), 0.05 g.

$[Pd(C_6H_4\text{-}C(=N\text{-}OH)C_6H_5,2\text{-}C,N)L(PPh_3)]ClO_4$ (**8**) and $[Pd(C_6H_4CH_2NMe_2,2\text{-}C,N)L(PPh_3)]ClO_4$ (**9**) were obtained similarly.

Results and Discussion

When the electron rich olefin and the cyclopalladated halogen-bridged dimeric complex were mixed in *m*-xylene under reflux, the reaction mixture immediately changed from pale yellow to pale orange or reddish violet and then to a black suspension owing to partial decomposition. A similarly highly colored state has also been observed in the reaction between the olefin and di-μ-chloro-dichlorobis(trialkylphosphine)dipalladium(II) or -diplatinum(II) by Lappert *et al.*[2] They assumed the formation of an intermediate π-complex, followed by cleavage of the double bond to yield a carbene complex.



acetophenone oxime, 2-*C,N*; **1**, **4**, and **7**
benzophenone oxime, 2-*C,N*; **2**, **5**, and **8**
N,N-dimethylbenzylamine, 2-*C,N*; **3a**, **6**, and **9**

TABLE 2. IR DATA OF THE Pd(II) CARBENE COMPLEXES[a]

	ν(O-H)[b]	ν(C_ϕ-N)[c,d]	Far-IR data[c,e]
1	3190	1270	431s, (315sh, $\underline{\text{295s}}$, 286sh, 277sh), 240w
2	3170	1275	429s, 315—303s, 240s
3b		1280	426m, 358w, (315sh, $\underline{\text{289s}}$), 253w
4	3225	1280	430s, 315w, 285—277w
5	3200	1272	428s, 311—295m, 245w
6		1275	421m, 357w, 314w, 264w
7	3480 3230	1274	423m, 275w
8	3470 3240	1270	426m
9		1275	429s, 251w

a) Values in cm^{-1}. b) In Nujol mull. c) In KBr disc. d) ν($C_{aromatic}$-N). e) Underlined numbers refer to ν(Pd-Cl).

The complexes, **1**, **2**, and **3a** underwent halogen metathesis with lithium bromide to yield the corresponding bromo-derivatives, and reacted with triphenylphosphine affording **7**, **8**, and **9**, respectively. Tables 1, 2, and 3 give the yields, analytical data, and physical and spectroscopic properties of the complexes obtained in this study.

Complexes **1**, **2**, and **3a** exhibited low conductivities, indicating non-ionic character[8] (Table 1). However, **7**, **8**, and **9** have been ascribed to the cationic complexes on the basis of high conductivities.[8] In the conversion of **1**, **2**, and **3a** to **7**, **8**, and **9**, respectively, triphenylphosphine displaced the chlorine atom of the initial complex and the nitrogen donor remained coordinated to the central metal,

Table 3. ^{1}H-NMR data of the carbene complexes

	NMR data$^{a,b)}$, δ value, ppm				
	$\mathrm{O\underline{H}}$	Aromatic	$\mathrm{NC\underline{H}_2C\underline{H}_2N}$	$\mathrm{C\underline{H}_2NMe_2}$	$\mathrm{C\underline{H}_3}$
1	9.85(s)	8.05—6.65(c)	4.34(c)		2.08(s)
2	10.07(s)	8.20—6.60(c)	4.45(c)		2.10(s , $\mathrm{Me_2CO}$)
3b$^{c)}$		8.28—6.58(c)	4.33(c)	3.61(s)	2.59(s)
4	9.49(s)	8.14—6.72(c)	4.39(s)		2.12(s)
5	9.72(s)	8.33—6.77(c)	4.53(s)		
6$^{c)}$		8.28—6.66(c)	4.34(s)	3.66(s)	2.64(s)

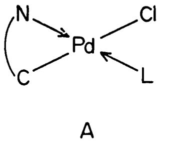
a) δ value relative to TMS; in $\mathrm{CD_2Cl_2}$, unless noted elsewhere. b) s=singlet, c=complex. c) In $\mathrm{CDCl_3}$.

^{13}C-NMR spectrum of **3b** in $\mathrm{CDCl_3}$ showed a resonance at δ 201.6 from TMS, assignable to a carbene carbon atom. As for the 1,3-diphenylimidazolidin-2-ylidene ligand, two methylene carbons showed a single resonance, indicating that the $\mathrm{N-C_{carbene}-N}$ plane was perpendicular to the coordination plane of the palladium atom and the *N*-substituted two phenyl carbons were spectroscopically equivalent. In the range of δ 137 to 160, the spectrum also gave resonances at δ 149.1, 147.8, and 141.8, which are assignable to three kinds of quarternary carbon atoms, methylene- and palladium-substituted phenylene carbons (1-C and 2-C) in the cyclopalladated moiety and *N*-substituted two phenyl carbons in the carbene ligand.$^{9)}$

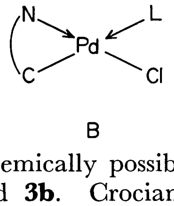
On the basis of these facts, complex **3b** was ascribed to a new carbene complex which retained the cyclopalladated chelate structure of the starting compound. The complexes, **1** and **2** also exhibited chemical and spectroscopic properties similar to **3b**, and were assumed to have a structure similar to **3b**. These carbene complexes containing the cyclometallated aryl group are stable in air at room temperature.

Four methylene protons of the imidazolidin-2-ylidene group were represented by an A_2B_2 spin system in the ^{1}H-NMR spectra and showed a complex signal in chloro-type complexes, **1**, **2**, and **3b**, as shown in Table 3. Each of the bromo-type complexes, **4**, **5**, and **6**, gave virtually a singlet in the A_4 limit for the methylene protons.

The IR spectra of these nine carbene complexes showed a strong band near 1275 cm^{-1} for $\nu(\mathrm{C_{aromatic}-N})$ of the 1,3-diphenylimidazolidin-2-ylidene ligand. Two bands were observed in the range 3200—3500 cm^{-1} in **7** and **8**. The lower frequency band was tentatively assigned as a hydrogen-bonding ν(O–H) of an oxime group and the sharp higher frequency band as that of a non-hydrogen-bonding ν(O–H).$^{10)}$



A



B

Two structures are stereochemically possible for the carbene complexes, **1**, **2**, and **3b**. Crociani *et al.*$^{11)}$ studied the ν(Pd–Cl) frequencies of mononuclear complexes derived from di-μ-chloro-bis(*N*,*N*-dimethylbenzylamine, 2-*C*,*N*)dipalladium(II) or related complexes and donor ligands. They reported that the ν(Pd–Cl) frequency *trans* to a tertiary amine-nitrogen donor fell in the range of 353—321 cm^{-1} and the ν(Pd–Cl) frequency *trans* to an aryl group in the range of 299—280 cm^{-1}, and correlated the differences of these frequencies to that of the *trans* influence of the respective ligands. In consideration of the data reported here and related ones,$^{12,13)}$ structure A has been assigned for complexes **1** and **3b**. No evidence supporting the presence of the other geometrical isomer B for **1** and **3b** were found in the NMR and IR (450—200 cm^{-1}) spectra.

The ν(Pd–Cl) band for **2** could not be clearly assigned. However, **2** also appears to have structure A, since no band was observed in the range of 353—321 cm^{-1}. Obscurity of the ν(Pd–Cl) assignment of **2** may be accounted for either by overlapping of the weak ν(Pd–Cl) band with strong bands at 303—315 cm^{-1}, or by the large shift of the ν(Pd–Cl) frequency towards the lower wavenumber probably due to the intramolecular hydrogen-bonding of chlorine.

We are grateful to Professor Keinosuke Hamada and Mr. Hirofumi Morishita, Nagasaki University, for their help in the far IR measurements.

References

1) H. W. Wanzlick, *Angew. Chem.*, **80**, 809 (1968).

2) D. J. Cardin, B. Cetinkaya, E. Cetinkaya, and M. F. Lappert, *J. Chem. Soc., Dalton Trans.*, **1973**, 514.

3) M. Onishi, Y. Ohama, K. Sugimura, and K. Hiraki, *Chem. Lett.*, **1976**, 955.

4) The authors thank Dr. Makoto Takagi, Kyushu University for helpful discussions on ^{13}C-NMR spectra.

5) H. Onoue, K. Minami, and K. Nakagawa, *Bull. Chem. Soc. Jpn.*, **43**, 3480 (1970).

6) A. C. Cope and E. C. Friedrich, *J. Am. Chem. Soc.*, **90**, 909 (1968).

7) H. W. Wanzlick, *Org. Synth.*, **47**, 14 (1967).

8) W. J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).

9) ^{13}C-NMR spectrum of di-μ-chloro-bis(*N*,*N*-dimethylbenzylamine, 2-*C*,*N*)dipalladium(II) in $\mathrm{CDCl_3}$ showed two resonances at δ 147.1, and 143.1 for quarternary methylene- and palladium-substituted phenylene carbons in the range of δ 137 to 160.

10) Complexes, **7** and **8** are sparingly soluble in carbon tetrachloride and chloroform, and detailed examination of the hydrogen-bonding of these cationic complexes were not obtained.

11) B. Crociani, T. Boschi, R. Pietropaolo, and U. Belluco, *J. Chem. Soc., A*, **1970**, 531.

12) J. Dehand, M. Pfeffer, and M. Zinsius, *Inorg. Chim. Acta*, **13**, 229 (1975).

13) K. Suzuki and H. Yamamoto, *J. Organomet. Chem.*, **54**, 385 (1973).