September, 1979] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (9), 2531—2534 (1979) 2531

Preparations and Characterization of Cyclopalladated Complexes of 1-Ethyl-2-phenylimidazole

Katsuma Hiraki,* Yoshio Fuchita,* Hiroshi Nakaya, and Shinji Takakura
Department of Industrial Chemistry, Faculty of Engineering, Nagasaki University, Bunkyo-machi, Nagasaki 852

(Received November 25, 1978)

Reactions of 1-ethyl-2-phenylimidazole (Hepim) with lithium tetrachloropalladate(II) and palladium(II) acetate give dichlorobis(1-ethyl-2-phenylimidazole, 3-*N*) palladium(II) and a new cyclopalladated binuclear complex, di-μ-acetato-bis[2-(1′-ethyl-2′-imidazolyl)phenyl, 1-*C*, 3′-*N*]dipalladium(II), respectively. The latter complex is readily converted by a metathetical reaction with sodium chloride into a chloro-bridged analogue, $[\{PdCl(epim)\}_2]$. The chloro-bridged complex reacts with 4-picoline, tertiary phosphines, thallium(I) acetylacetonate, sodium diethyldithiocarbamate, and 2,2′-bipyridyl to give the corresponding mononuclear cyclopalladated complexes. All the complexes prepared in this study are characterized by means of IR, ^{1}H-NMR, and mass spectroscopies.

Cyclometallation reactions have recently received considerable attention in view of the formation of stable transition metal-carbon σ-bonds[1—3] and availabilities for the organic syntheses.[3] With respect to the cyclometallation reactions involving aryl-substituted five-membered heterocycles, several works have been reported concerning 1-phenylpyrazole,[4—6] 2,4-diphenyloxazole,[4] and 2-phenyl-3*H*-indole.[7]

It is interesting to investigate the susceptibility to the cyclometallation reactions of aryl-substituted heterocycles. In this paper, we report the cyclopalladation reaction of 1-ethyl-2-phenylimidazole (Hepim) resulting in the formation of an acetato-bridged binuclear complex, a metathetical reaction of the acetato complex into a chloro-bridged one, and the bridge-splitting reactions of the latter complex with 4-picoline (pic), tertiary phosphines, thallium(I) acetylacetonate [Tl(acac)], sodium diethyldithiocarbamate [Na(dedc)], and 2,2′-bipyridyl (bpy).

Experimental

Materials and General Procedures. All the experiments were carried out in an atmosphere of dry dinitrogen. Solvents were dried by usual methods and distilled. 1-Ethyl-2-phenylimidazole,[8] diphenyl-*p*-tolylphosphine,[9] Tl(acac),[10] and thallium(I) cyclopentadienide[11] were prepared according to the published procedures.

IR spectra were measured on a Hitachi model 285 and a Shimadzu IR 450 spectrophotometers. ^{1}H- and ^{13}C-NMR spectra were recorded on JEOL JNM-MH-100 and PFT-100 spectrometers, respectively, using tetramethylsilane as an internal standard. Conductivity measurement was carried out for 1.0×10^{-3} M acetonitrile solution at 25 °C on a Toa Electronics CM-6A conductance meter. Melting points were determined with a Yanaco micro melting point apparatus and are uncorrected. Mass spectra were obtained with a Nichiden-Varian TE-600 gas chromatograph-mass spectrometer.

Preparation of $[PdCl_2(Hepim)_2]$ ***1***. 1-Ethyl-2-phenylimidazole (6.56 mmol) in 30 ml of methanol was added to a solution of lithium tetrachloropalladate(II) (3.28 mmol) in 30 ml of methanol. A yellow precipitate formed immediately, which was filtered after standing for 20 h at room temperature and washed with methanol several times. Recrystallization from boiling toluene gave 0.75 g of **1** as yellow needles; yield 44%, mp 242—244 °C (dec).

Preparation of $[\{Pd(O_2CCH_3)(epim)\}_2]$ ***2***. To a solution of palladium(II) acetate (17.8 mmol) in 50 ml of acetic acid was added Hepim (21.1 mmol) in 30 ml of acetic acid at room temperature. After refluxing for 30 min, the resulting black mixture was diluted with water and extracted with eight 50 ml portions of dichloromethane. The combined brownish-yellow extracts were concentrated and chromatographed on silica gel. A yellow band eluted by dichloromethane/ethanol (4/1) was collected and the solvent was evaporated. Recrystallization from boiling benzene gave 2.5 g of **2** as yellow crystals; yield 42%, mp 180—219 °C(dec).

Preparation of $[\{PdCl(epim)\}_2]$ ***3***. Sodium chloride (7.4 mmol) in 60 ml of water was added to a solution of **2** (3.7 mmol) in 200 ml of acetone. A pale yellow precipitate formed immediately, which was filtered after stirring for 20 h at room temperature and washed with water and diethyl ether. Yield 2.0 g, 86%; mp 274—278 °C(dec).

Reaction of ***3*** *with pic.* 4-Picoline (5.11 mmol) was added to a suspension of **3** (0.64 mmol) in 10 ml of dichloromethane. A clear solution formed immediately, which was concentrated after stirring for 5 h at room temperature. Addition of pentane gave 0.35 g of [PdCl(epim)(pic)] **4** as off white crystals, yield 67%, mp 161—162 °C(dec).

Reactions of ***3*** *with Triphenylphosphine and Diphenyl-*p*-tolylphosphine.* These reactions were carried out in the same way as described for **4**, and off white crystals, $[PdCl(epim)(PPh_3)]$ **5** and $[PdCl(epim)(PPh_2–C_6H_4–CH_3-p)]$ **6** were produced: **5**, yield 86%, mp 232—235 °C(dec); **6**, yield 57%, mp 232—234 °C(dec).

Reaction of ***6*** *with Lithium Bromide.* An acetone suspension containing **6** (0.40 mmol) and lithium bromide monohydrate (2.00 mmol) was refluxed for 10 h. The mixture was filtered and the filter residue was washed with water and diethyl ether. Recrystallization from dichloromethane and pentane gave 0.16 g of $[PdBr(epim)(PPh_2–C_6H_4–CH_3-p)]$ **7** as pale yellow crystals; yield 74%, mp 229—231 °C(dec).

Reaction of ***3*** *with Tl(acac).* Thallium(I) acetylacetonate (1.54 mmol) was added to a suspension of **3** (0.64 mmol) in 10 ml of dichloromethane, and the mixture was stirred for 20 h at room temperature. The mixture was filtered and subsequent evaporation of the solvent gave a pale yellow oil. The oil was purified by passing through a short silica gel columm with dichloromethane, and 0.3 g of [Pd(acac)-(epim)] **8** was obtained as pale yellow crystals: yield 63%; mp 187—190 °C(dec); Found: M$^+$, 376. Calcd for $C_{16}H_{18}N_2O_2Pd$: M$^+$, 376.

Reaction of ***3*** *with Na(dedc).* An ethanol suspension containing Na(dedc) (1.92 mmol) and **3** (0.80 mmol) was stirred for 20 h at room temperature. The mixture was evaporated to dryness and the resulting solid was extracted with dichloromethane. Addition of hexane to the extract afforded pale yellow crystals, [Pd(dedc)(epim)] **9**: yield 78%; mp 178—181 °C(dec); Found: M+, 425. Calcd for $C_{16}H_{21}N_3S_2Pd$: M+, 425.

*Reaction of **3** with bpy.* 2,2′-Bipyridyl (1.76 mmol) was added to a suspension of **3** (0.80 mmol) in 20 ml of methanol. A yellow clear solution immediately formed. After stirring for 4 h at room temperature, the solution was treated with sodium perchlorate monohydrate (1.60 mmol) to give 1.13 g of $[Pd(epim)(bpy)]ClO_4$ **10** as yellow crystals; yield 90%, mp 276—277 °C(dec).

Results and Discussion

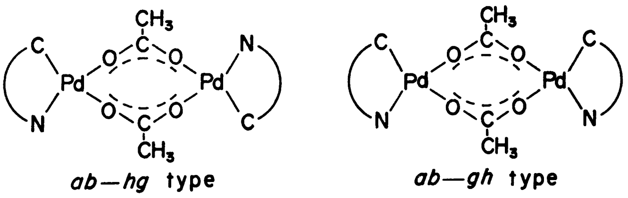
Elemental analyses and ^{1}H-NMR spectra of all the new complexes prepared in this study are summarized in Table 1.

The reaction of Hepim with lithium tetrachloropalladate(II) in methanol at room temperature afforded dichlorobis(1-ethyl-2-phenylimidazole, 3-*N*)palladium(II) **1** as yellow needles. In the ^{1}H-NMR spectrum of **1**, the phenyl protons of Hepim appeared as two multiplets at δ 7.4—7.7 (6H) and 7.75—8.0 (4H), similar to the signals of uncoordinated Hepim {two multiplets at δ 7.3—7.5 (3H) and 7.5—7.65 (2H)}. This indicates the presence of unsubstituted phenyl group. Judging from the results of elemental analysis and the ^{1}H-NMR spectrum, **1** contained two moles of Hepim as ligands coordinated only with a nitrogen donor site, but not a cyclopalladated moiety.

$$Li_2[PdCl_4] + 2Hepim \xrightarrow[\text{r.t.}]{\text{methanol}} [PdCl_2(Hepim)_2]\ \mathbf{1} + 2LiCl$$

1-Ethyl-2-phenylimidazole also reacted with palladium(II) acetate in refluxing acetic acid to produce a new complex **2**, whose IR spectrum exhibited two strong absorption bands due to bridging acetato ligand at 1570 and 1410 cm^{-1}.[13] On the basis of elemental analysis and the characterization of the derivatives from **2** as stated later, **2** was assigned to a binuclear cyclopalladated complex, di-*μ*-acetato-bis[2-(1′-ethyl-2′-imidazolyl)phenyl, 1-*C*, 3′-*N*]dipalladium(II). It is noteworthy that Hepim reacted with tetrachloropalladate(II) ion to give only the addition product **1** and with palladium(II) acetate to afford the cyclopalladated complex **2**, similar to the case of *N*-benzylideneaniline.[13] As for the ^{1}H-NMR spectrum of **2**, the methyl resonance of bridging acetato ligand showed a sharp singlet at δ 2.20 together with two weak resonances at δ 2.12 and 2.29. These resonances were

$$2[Pd(O_2CCH_3)_2] + 2Hepim \xrightarrow[\text{reflux}]{\text{acetic acid}} [\{Pd(O_2CCH_3)(epim)\}_2]\ \mathbf{2} + 2CH_3CO_2H$$



ab—hg type *ab—gh* type

Fig. 1. Structural isomers of **2**.

(C, N = (epim,1-*C*,3′-*N*).

Table 1. Elemental analyses and ^{1}H-NMR spectra of the palladium complexes

	Elemental analyses a)			^{1}H-NMR spectra (δ-value from TMS) b)					
	(%)			epim ring c)		epim ethyl d)		Other ligand	
	C	H	N	4′-H	5′-H	$-CH_2-$	$-CH_3$	$-CH_3$	Others
1	50.52 (50.64)	4.59 (4.64)	10.67 (10.74)	7.16(d)	7.00(d)	3.84(q)	1.25(t)	—	—
2	46.86 (46.38)	4.25 (4.19)	7.94 (8.32)	6.39(d)	6.23(d)	3.85(q)	1.25(t)	2.20(s) e)	—
3	42.24 (42.20)	3.45 (3.54)	8.79 (8.95)	—	—	—	—	—	—
4	49.83 (50.27)	4.40 (4.47)	10.20 (10.34)	7.36(d)	6.84(d)	4.28(q)	1.48(t)	2.40(s)	8.72(dd) f) (pic-H_α)
5	60.86 (60.54)	4.64 (4.55)	4.49 (4.87)	— g)	6.81(d)	4.30(q)	1.54(t)	—	—
6	60.93 (61.14)	4.94 (4.79)	4.77 (4.75)	— g)	6.81(d)	4.30(q)	1.54(t)	2.34(s)	—
7	56.32 (56.85)	4.37 (4.45)	4.33 (4.42)	— g)	6.81(d)	4.30(q)	1.54(t)	2.34(s)	—
8	50.66 (51.01)	4.84 (4.82)	7.21 (7.44)	7.08(d)	6.75(d)	4.26(q)	1.51(t)	2.02(s) 2.08(s)	5.73(s) (≡CH)
9	45.48 (45.12)	5.10 (4.97)	9.81 (9.87)	6.87(d)	6.76(d)	4.28(q)	1.48(t)	1.28(t) h) 1.32(t) h)	3.841(q) h) ($-CH_2-$)
10	47.59 (47.30)	3.54 (3.59)	10.38 (10.51)	—	—	—	—	—	—

a) Calculated values in parentheses. b) In $CDCl_3$ except for **1** and **4** (CD_2Cl_2); see the text about the aromatic protons of **4**, **8**, and **9**. s=singlet, d=doublet, t=triplet, q=quartet. c) $J_{4',5'}=1.5$ Hz. d) $J=8.0$ Hz. e) See the text. f) $J_{\alpha,\beta}=5.0$ Hz, $J_{\alpha,\beta'}=1.5$ Hz. See Ref. 12. g) Not distinguished owing to overlapping with the aromatic protons. h) $J=7.0$ Hz.

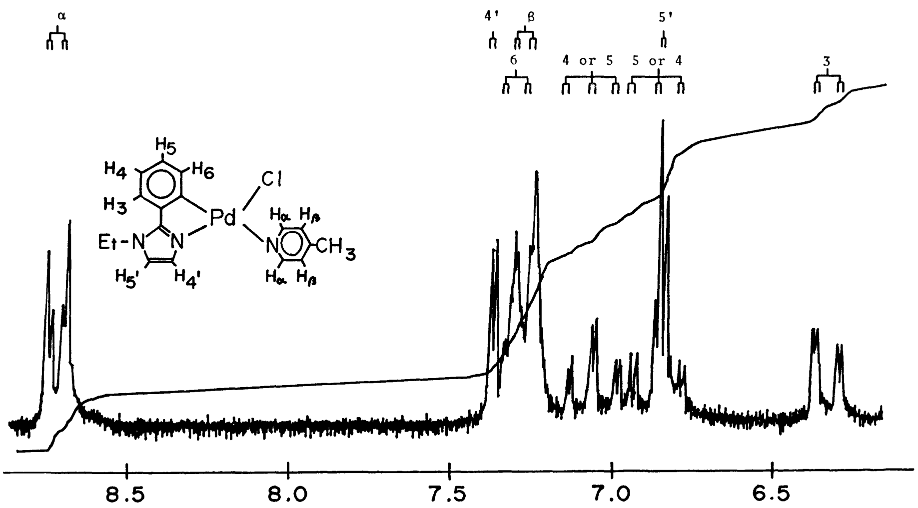


Fig. 2. ^{1}H-NMR spectrum of **4** in CD_2Cl_2 solution (δ-value from TMS).

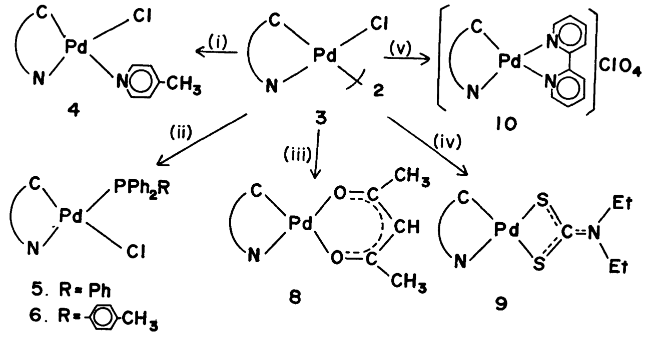
ascribed to two structural isomers as shown in Fig. 1;[14] the former was to two magnetically equivalent methyl protons in an *ab-hg* type and the latters were to non-equivalent methyl ones in an *ab-gh* type (the isomer ratio *ab-hg* : *ab-gh*=5 : 1, approximately).

Complex **2** was readily converted by metathetical reaction with sodium chloride in acetone into the chloro-bridged analogue, [{PdCl(epim)}$_2$] **3**. The

$$[\{Pd(O_2CCH_3)(epim)\}_2] + 2NaCl \xrightarrow[\text{r.t.}]{\text{acetone}} [\{PdCl(epim)\}_2]\ \mathbf{3} + 2CH_3CO_2Na$$

^{1}H-NMR spectrum of **3** could not be measured owing to its insolubility in usual organic solvents. However, **3** underwent typical bridge-splitting reactions with various reagents as shown in Scheme 1. Reactions of **3** with unidentate ligands, pic, triphenylphosphine, and diphenyl-*p*-tolylphosphine gave neutral mononuclear complexes **4**, **5**, and **6**, respectively.

The ^{1}H-NMR spectrum of **4** (Fig. 2) showed a typical ABCD system characteristic of the *o*-phenylene protons in the 2-(1'-ethyl-2'-imidazolyl)phenyl moiety, differing from the aromatic region of Hepim or **1**. The 6-H of *o*-phenylene group appeared at δ *ca.* 7.3, overlapping with two H_β protons of the picoline ligand (total intensity 3H). The 4- or 5-H was observed at δ 7.06 (1H) or 6.86 (1H) as a double triplet due to coupling with other ring protons. The 3-H appeared at δ 6.33 (1H) as a double doublet due to coupling with 4- and 5-H. The coupling constants were $^3J_{HH}$=7.5 Hz and $^4J_{HH}$=1.5 Hz. These results indicate unambiguously that **4** has the cyclopalladated structure of epim.



Scheme 1. Bridge-splitting reactions of **3**. Reagents; (i) pic, (ii) PPh_2Ph(for **5**) or PPh_2–C_6H_4–CH_3-*p*(for **6**), (iii) Tl(acac), (iv) Na(dedc), (v) bpy, $NaClO_4$.

(C N) = (epim,1-*C*,3'-*N*).

In the far-IR spectrum of **6**, a band at 304 cm^{-1} was assigned to ν(Pd–Cl) frequency in comparison with the corresponding bromo derivative **7**. On the other hand, **4** showed two bands at 316 and 266 cm^{-1} in the range of 350—250 cm^{-1}. The former was assigned to ν(Pd–Cl) frequency and the latter to the palladium-nitrogen stretching one.[15] As for the configuration of **4**, **5**, or **6**, there are two possible isomers as shown in Fig. 3. Crociani *et al.* reported that the ν(Pd–Cl) frequencies trans to an aromatic nitrogen atom and an aryl-carbon one fell in the range of 353—321 and 299—280 cm^{-1}, respectively.[15] Moreover, ^{1}H-decoupled ^{13}C-NMR spectrum of **5** in $CDCl_3$ exhibited a doublet at δ 151.9, which was due to coupling with ^{31}P nucleus ($^2J_{CP}$=27.6 Hz) and assignable to palladium-substituted *o*-phenylene carbon (1-C). This small coupling constant reveals that triphenylphosphine ligand is located at cis position to the 1-C.[16] On the basis of both far-IR and ^{13}C-NMR data, **5** and **6** were ascribed to configuration B. However, **4** could not be assigned whether it had the configuration A or B only from a far-IR spectrum datum.

In the ^{1}H-decoupled ^{13}C-NMR spectrum of **5**, the 2'-, 4'-, and 5'-C's of imidazole ring were observed

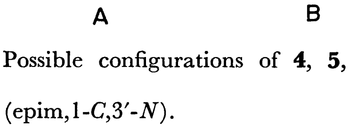


Fig. 3. Possible configurations of **4**, **5**, and **6**.

(C N) = (epim,1-*C*,3'-*N*).

at δ 127.2 (doublet, $^3J_{CP}$=4.9 Hz), 139.6 (doublet; $^3J_{CP}$=12.2 Hz, $^1J_{CH}$=146 Hz), and 132.2 (singlet),[17] respectively. A singlet at δ 137.7 was ascribed to imidazole-substituted *o*-phenylene carbon (2-C), and other four carbons (3-, 4-, 5-, and 6-C) upon the phenylene group appeared as four singlets at δ 119.2, 121.7, 123.9, or 126.5. These six kinds of the *o*-phenylene carbons also confirm that **5** contains the cyclopalladated epim structure.

Thallium(I) acetylacetonate and Na(dedc) reacted with **3** to produce neutral complexes **8** and **9**, respectively. The ^{1}H-NMR spectrum of **8** afforded two multiplets; one(1H) at δ 7.57—7.70, assignable to 6-H, the other (4H) at δ 6.99—7.26, which corresponded to 3-, 4-, and 5-H's and overlapped with 4′-H of the imidazole ring. The ^{1}H-NMR spectrum of **9** exhibited a complicated pattern due to the *o*-phenylene protons (4H) in the region of δ 6.95—7.36. The mass spectrometry gave peaks at *m/e* 376 (parent ion corresponding to ^{106}Pd) and 277 (loss of acac) for **8**, and at *m/e* 425 (parent ion corresponding to ^{106}Pd) and 277 (loss of dedc) for **9**. These results confirm the presence of the cyclopalladated structure of epim in both **8** and **9**.

As for the ^{1}H-NMR spectrum of **9**, two methyl protons of diethyldithiocarbamato ligand were unequivalent, indicating that a carbon-nitrogen double bond character is present in this ligand.[18] On the other hand, the methylene protons were observed as one quartet, which was considered to arise from an accidental magnetic degeneracy.

Complex **3** also reacted with bpy in the presence of sodium perchlorate to form a complex **10**. The IR spectrum of **10** showed a strong ν(Cl–O) band at 1080 cm^{-1}, characteristic of perchlorate anion. Molar conductivity (Λ_M=140 Ω^{-1} cm^2 mol^{-1}) in acetonitrile solution indicates that **10** is a uni-univalent electrolyte. The product from the reaction of **3** with thallium(I) cyclopentadienide was too unstable to be isolated in a pure state.

We wish to express our gratitude to Professor Keinosuke Hamada and Mr. Hirofumi Morishita of Nagasaki University for the far-IR measurements, and to Dr. Hideomi Koinuma, the University of Tokyo, for the ^{13}C-NMR measurements, and also to Mrs. Hisako Mazume and Miss Yumi Kojima of Nagasaki University for their technical assistances.

References

1) M. Nonoyama, *Kagaku No Ryoiki*, **28**, 674 (1974).
2) J. Dehand and M. Pfeffer, *Coord. Chem. Rev.*, **18**, 327 (1976).
3) M. I. Bruce, *Angew. Chem. Int. Ed. Engl.*, **16**, 73 (1977).
4) M. I. Bruce, B. L. Goodall, and I. Matsuda, *Aust. J. Chem.*, **28**, 1259 (1975).
5) M. Nonoyama, *J. Organomet. Chem.*, **86**, 263 (1975).
6) S. Trofimenko, *Inorg. Chem.*, **12**, 1215 (1973).
7) Y. A. Ustynyuk, V. A. Chertor, and I. V. Barinov, *J. Organomet. Chem.*, **19**, C53 (1971).
8) H. J. J. Loozen, J. J. M. Drouen, and O. Piepers, *J. Org. Chem.*, **40**, 3279 (1975).
9) J. J. Monagle, J. V. Mangehauer, and D. A. Jones, Jr., *J. Org. Chem.*, **32**, 2477 (1967).
10) W. H. Nelson, W. J. Randall, and D. F. Martin, *Inorg. Syn.*, **9**, 53 (1971).
11) H. Meister, *Angew. Chem.*, **69**, 533 (1957).
12) T. J. Batterham, "NMR Spectra of Simple Heterocycles," ed by E. C. Taylor and A. Weissberger, John Wiley & Sons, New York (1973), Chap. 10.
13) H. Onoue and I. Moritani, *J. Organomet. Chem.*, **43**, 431 (1972).
14) A. J. Deeming and I. P. Rothwell, *J. Chem. Soc., Chem. Commun.*, **1978**, 344.
15) B. Crociani, T. Boschi, R. Pietropaolo, and U. Belluco, *J. Chem. Soc., A*, **1970**, 531.
16) D. J. Cardin, B. Cetinkaya, E. Cetinkaya, and M. F. Lappert, *J. Chem. Soc., Dalton Trans.*, **1973**, 1982.

[17] $^1J_{CH}$ of 5′-*C* was not detected owing to overlapping with the phenyl protons of PPh$_3$.

18) M. C. Cornock and T. A. Stephenson, *J. Chem. Soc., Dalton Trans.*, **1977**, 501.