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SYNTHESES AND CHARACTERIZATION OF CYCLOPALLADATED COMPLEXES OF 2-PHENYLTHIAZOLE

KATSUMA HIRAKI *, YOSHIO FUCHITA * and SHINJI TAKAKURA

Department of Industrial Chemistry, Faculty of Engineering, Bunkyo-machi, Nagasaki 852 (Japan)

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Summary

2-Phenylthiazole reacts with palladium(II) acetate to give a new cyclopalladated, acetato-bridged binuclear complex, $[\{Pd(O_2CMe)(phtz)\}_2]$ [phtz = 2-(2′-thiazolyl)phenyl-1-*C*,*N*]. A chloro-bridged analogue, $[\{PdCl(phtz)\}_2]$, produced by the reaction of the acetato-bridged complex with sodium chloride, undergoes bridge-splitting reactions with triphenylphosphine, 3,5-lutidine, and thallium(I) acetylacetonate to give the corresponding mononuclear cyclopalladated complexes. All the new complexes were characterized by means of elemental analysis, and IR and NMR spectroscopy. Reactions of $[\{PdCl(phtz)\}_2]$ with methyl vinyl ketone and styrene afford 2-phenylthiazole and 2-(2′-thiazolyl)stilbene, respectively.

Introduction

In recent years increasing attention has been paid to cyclometallated complexes in view of the fact that they show useful reactivity [1]. Thus, disubstituted acetylenes and carbon monoxide insert into the M—C σ bond of the cyclometallated complexes to afford substituted vinylpalladium(II) complexes [2,3] and unusual heterocyclic compounds [1,4], respectively.

Previously, the cyclopalladation of 1-ethyl-2-phenylimidazole and the reactions of the cyclopalladated complex with various reagents were reported from our laboratory [5]. In continuation of our studies of cyclopalladation reactions of aryl-substituted five-membered heterocycles, we report here on the synthesis of an acetato-bridged binuclear cyclopalladated complex, $[\{Pd(O_2CMe)(phtz)\}_2]$ (II) [phtz = 2-(2′-thiazolyl)phenyl-1-*C*,*N*], formed by a reaction between 2-phenylthiazole (Hphtz) and palladium(II) acetate, and on some new complexes derived from II. Reactions between $[\{PdCl(phtz)\}_2]$ and a few vinyl compounds also were examined. The cyclopalladated structure of the phtz

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moiety in these complexes was discussed on the basis of ^{1}H and ^{13}C NMR spectroscopy and of the formation of 2-(2′-thiazolyl)stilbene. Recently, Churchill et al. [6] reported the synthesis and crystal structures of acetato-bridged dimeric cyclopalladated complexes derived from 2-*p*-tolylbenzthiazole and 2-*p*-tolylbenzoxazole.

Experimental

General procedures

Thallium(I) acetylacetonate [Tl(acac)] [7] and Hphtz [8] were prepared according to the published methods. Melting points were determined on a Yanaco micro melting point apparatus and are uncorrected. IR spectra were recorded on a Hitachi 285 spectrophotometer. ^{1}H and ^{13}C NMR spectra were measured using JEOL JNM-MH-100 and PF-100 spectrometers, respectively.

Preparation of $[PdCl_2(Hphtz)_2]$ (I)

A reaction of Hphtz (2.26 mmol) and lithium tetrachloropalladate(II) (1.13 mmol) in 25 ml of methanol afforded a yellow precipitate immediately. After standing for 24 h at room temperature, the precipitate was filtered and washed with water and methanol. Recrystallization from dichloromethane and hexane gave 0.45 g of I as orange-yellow crystals.

Preparation of $[\{Pd(O_2CMe)(phtz)\}_2]$ (II)

An acetic acid suspension (20 ml) of palladium(II) acetate (4.45 mmol) and Hphtz (4.90 mmol) was heated under reflux for 45 min. The mixture was cooled, diluted with 20 ml of water, and extracted with five 20 ml portions of dichloromethane. The extracts were concentrated and chromatographed on a silica gel column (200 mesh, $12^{\phi} \times 200$ mm). A yellow band eluted by dichloromethane/ethanol (4/1) was collected and the solvent was removed. Recrystallization from boiling benzene gave 0.95 g of II as yellow crystals.

Preparation of $[\{PdCl(phtz)\}_2]$ (III)

Sodium chloride (3.68 mmol) and II (1.84 mmol) in a THF/H_2O (80 ml/20 ml) mixed solvent were stirred for 24 h at room temperature. The resulting yellow precipitate was collected and washed with water and diethyl ether to give 0.95 g of III.

Reactions of III with triphenylphosphine and 3,5-lutidine

A yellow solution was obtained by adding triphenylphosphine or 3,5-lutidine (lut) (0.50 mmol) to a suspensión of III (0.25 mmol) in dichloromethane (10 ml). After stirring for 24 h at room temperature, addition of hexane to the mixture gave $[PdCl(phtz)(PPh_3)]$ (IV) or [PdCl(phtz)(lut)] (V) as yellow crystals, respectively.

Reaction of III with thallium(I) acetylacetonate

A suspension containing III (0.50 mmol) and Tl(acac) (1.20 mmol) in dichloromethane (20 ml) was stirred for 24 h at room temperature. The mixture was filtered and the filtrate was passed through a silica gel column (200 mesh,

12$^{\phi}$ × 50 mm) with dichloromethane. The yellow fraction was evaporated to dryness to afford 0.20 g of [Pd(acac)(phtz)] (VI) as yellow crystals.

Reaction of III with methyl vinyl ketone

A suspension containing III (1.24 mmol), methyl vinyl ketone (6.21 mmol) and triethylamine (3.10 mmol) in toluene (10 ml) was refluxed for 8 h. The resulting palladium black was filtered and the filter cake was washed thoroughly with diethyl ether (40 ml). The orange solution thus obtained was evaporated in vacuo, and the oily residue was distilled at 2 mm Hg (bath 120°C) to yield 2-phenylthiazole; yield 56% based on III. ^{1}H NMR (CCl_4): δ 7.3 m (3 H), 7.46 q ($\Delta\delta$ = 0.59, $^3J_{HH}$ = 3.5 Hz, 2 H), 7.9 ppm m (2 H) [9]. Mass spectrum: *m/e* 162, 161, 160 ($P^+ + 1$, P^+, $P^+ - 1$).

Reaction of III with styrene

This reaction was carried out for 3 h in the same way as described above, except *m*-xylene was used as solvent. The oily residue thus obtained was chromatographed on silica gel (200 mesh, 15$^{\phi}$ × 100 mm). Pale yellow and orange yellow fractions were obtained by eluting with dichloromethane and acetone, respectively. *trans*-2-(2′-Thiazolyl)stilbene(VII) was obtained from the former fraction by recrystallizing twice from pentane. VII: Yield 10% (based on III). M.p. 101°C. ^{1}H NMR (CCl_4): δ 6.86 q ($\Delta\delta$ 0.36, $^3J_{HH}$ = 16 Hz, 2 H), 7.3 m (8 H), 7.52 s (2 H), 7.8 ppm m (2 H). Analytical data; Found: C, 77.27; H, 5.05; N, 5.06. Calcd. for $C_{17}H_{13}NS$: C, 77.53; H, 4.98; N, 5.32%. Mass spectrum; *m/e* 263 (P^+), 160 ($P^+ - C_2H_2Ph$).

The latter fraction was evaporated to dryness to give Hphtz as an orange oil in 11% yield (based on III). Its mass spectrum exhibited the same pattern as the authentic Hphtz sample.

Results and discussion

2-Phenylthiazole reacted with lithium tetrachloropalladate(II) in methanol at ambient temperature, or palladium(II) acetate in refluxing acetic acid to yield yellow crystalline products, I or II, respectively. An ^{1}H NMR spectrum of I and II could not be obtained owing to their poor solubility in common organic solvents. Complex I was assigned as an addition product, dichlorobis(2-phenylthiazole-*N*)palladium(II), on the basis of the similarity of its IR spectrum to that of Hphtz and by elemental analysis. The IR spectrum of II showed strong bands at 1560 and 1400 cm^{-1} due to asymmetric and symmetric COO stretching vibrations, indicating that II has bridging acetato ligands [10]. On the basis of the IR data and elemental analysis, together with the characterization of derivatives from II, this product was assigned as a new cyclopalladated binuclear complex, di-μ-acetato-bis[2-(2′-thiazolyl)phenyl-1-*C*,*N*]dipalladium(II). It is noteworthy that while Hphtz gives the addition product with tetrachloropalladate(II), it is susceptible to cyclopalladation with palladium(II) acetate, as reported for benzylideneaniline [10] and 1-ethyl-2-phenylimidazole [5]. Elemental analyses and some properties of the new complexes obtained in this study are summarized in Table 1.

Complex III, a chloro-bridged analogue to II, was obtained in good yield by

TABLE 1

ELEMENTAL ANALYSES AND SOME PROPERTIES OF THE PALLADIUM COMPLEXES

Complex	Yield (%)	Mp (°C) (dec)	Found (Calcd) (%)			^{1}H NMR spectra (δ/ppm) [a]	
			C	H	N	4′-H [b]	5′-H [b]
I	80	245—247	42.85 (43.26)	2.74 (2.82)	5.56 (5.61)	— [c]	— [c]
II	66	210—215	40.15 (40.57)	2.76 (2.79)	4.26 (4.32)	— [c]	— [c]
III	86	225—235	35.25 (35.79)	2.05 (2.00)	4.44 (4.64)	— [c]	— [c]
IV	67	225—232	57.56 (57.46)	3.86 (3.75)	2.38 (2.48)	8.48 d	— [d]
V	76	185—187	45.99 (46.96)	3.56 (3.69)	6.65 (6.85)	8.22 d	7.25 d
VI	56	172—174	45.72 (45.98)	3.57 (3.58)	3.77 (3.83)	7.81 d	7.18 d

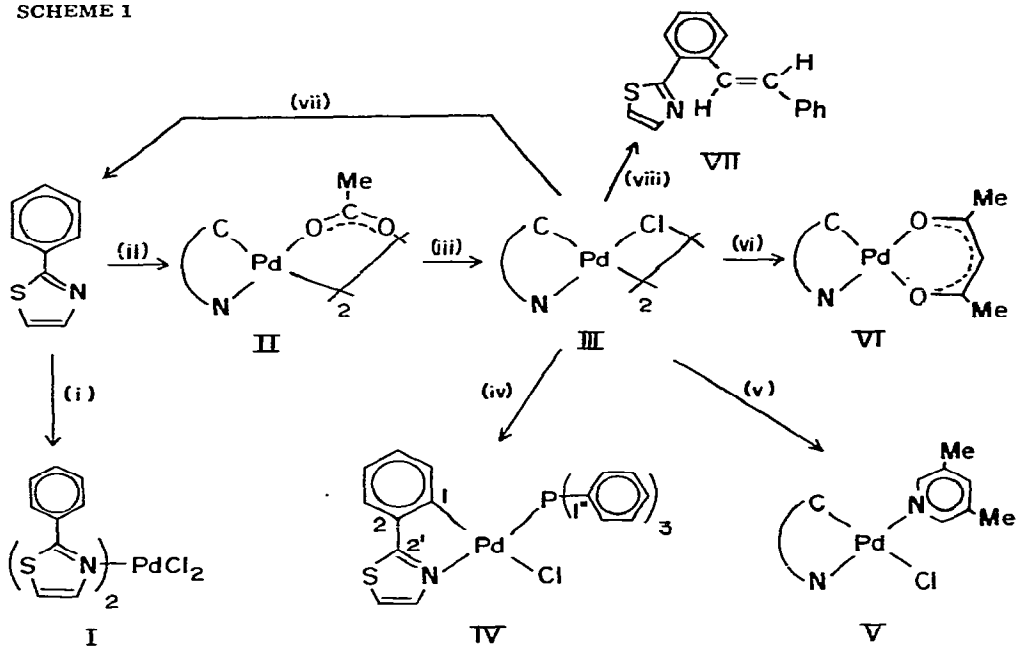
[a] Measured in $CDCl_3$ except for V (CD_2Cl_2). See the text concerning the aromatic protons. d = doublet. [b] $^3J_{4',5'}$ = 3.5 Hz. [c] Not measured owing its poor solubility in common organic solvents. [d] Not distinguished owing to overlapping with the aromatic protons.

the metathetical reaction of II with sodium chloride in THF/H_2O mixed solvent. The insoluble complex, III was converted to mononuclear cyclopalladated complexes, IV, V, and VI, by reactions with triphenylphosphine, lut, and Tl(acac), respectively (Scheme 1). These three complexes are fairly stable in air and are soluble in acetone, dichloromethane and chloroform, and insoluble in diethyl ether and hexane.

The ^{1}H-decoupled ^{13}C-NMR spectrum of IV was assigned refering to those of Hphtz and chloro[2-(1′-ethyl-2′-imidazolyl)phenyl-1-*C*,3′-*N*](triphenylphosphine)palladium(II) (VIII) * [5] (Table 2). Four quaternary carbon signals were observed as singlets at δ(C) 178.0, 151.8, 131.7, and 129.8 ppm, which were assignable to 2′-, 1-, 1″-, and 2-C's, respectively. These facts and the elemental analyses indicate unambiguously that IV has a cyclopalladated 2-(2′-thiazolyl)phenyl-1-*C*,*N* moiety, but no unpalladated Hphtz one. In view of the fact that 1-C did not actually couple with phosphorus-31 nucleus, it is concluded that the 1-C is situated at a *cis* position to the triphenylphosphine ligand [13]. The 4′- and 5′-C resonances appeared as doublets due to coupling with the phosphorus-31 nucleus at δ 138.7 ($^3J_{CP}$ = 10.3 Hz) and 115.1 ppm ($^4J_{CP}$ = 5.9 Hz), respectively. It is noteworthy that the coupling of the phosphorus-31 nucleus extended to the 3-C, which appeared at δ 129.0 ppm ($^4J_{CP}$ = 4.9 Hz) as a

* In the ^{13}C NMR spectrum of previously reported chloro[2-(1′-ethyl-2′-imidazolyl)phenyl-1-*C*,3′-*N*]-(triphenylphosphine)palladium(II) [5], there were errors about the assignments of the 1-C, 2′-C and 1″-C's. A doublet resonance at 151.9 ppm ($^2J_{CP}$ = 27.6 Hz) actually should be ascribed to two singlets at 152.5 and 151.4 ppm. The former resonance should be attributed to 1-C and the latter one should be ascribed to 2′-C. A doublet signal at δ 127.2 ppm ($^1J_{CP}$ = 4.9 Hz) should be assigned to 1″-C's of triphenylphosphine, but not to 2′-C. Moreover, two singlets at δ 119.2 and 132.2 ppm were assigned to 5′-C and one of the phenylene carbons, respectively, different from the assignment in ref. 5.

SCHEME 1



CYCLOPALLADATION REACTION OF 2-PHENYLTHIAZOLE

$\widehat{C\,N}$ = 2-(2′-thiazolyl)phenyl-1-*C*,*N*. (i) $Li_2[PdCl_4]$. (ii) $Pd(OAc)_2$. (iii) NaCl. (iv) PPh_3. (v) 3,5-Lutidine. (vi) Tl(acac). (vii) Methyl vinyl ketone. (viii) Styrene (followed by the formation of Hphtz).

doublet. As for the ^{1}H NMR spectrum of IV, a doublet at δ 8.48 ppm ($^3J_{HH}$ = 3.5 Hz) was assigned to 4′-H of thiazole ring, whereas other protons of the phtz moiety were obscured because of overlapping with phenyl protons of triphenylphosphine.

In contrast to the complicated aromatic proton signals in the NMR spectrum of IV, the ^{1}H NMR spectrum of V (Fig. 1) showed four separated *o*-phenylene proton resonances. Two double doublets attributable to 3-H and 6-H's were observed at δ 7.41 and 6.26 ppm ($^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 2 Hz), respectively, and two double triplets ascribable to 4- and 5-H's appeared at δ 7.07 and 7.00 ppm. These results also confirm the cyclopalladated structure of the phtz moiety in V. The 6-H resonance, observed at considerably higher field, is probably attributable to the anisotropic shielding from the ring current of the adjacent lutidine ring * [14]. This consideration suggested that lutidine is situated *cis* to the palladium-substituted carbon (1-C), similarly to IV.

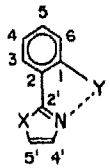
The IR spectrum of VI showed two strong absorptions at 1570 and 1500 cm^{-1} due to coupled C=O and C=C stretching modes of *O*,*O*′-chelating acac

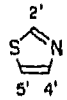
* In the previous paper [5], the 3-H and 6-H of the *o*-phenylene protons in chloro[2-(1′-ethyl-2′-imidazolyl)phenyl-1-*C*,3′-*N*](4-picoline)palladium(II) were erroneously assigned to the double doublets at δ 6.33 and ca. 7.3 ppm, respectively. In view of the fact that the 6-H shifts to considerably higher field due to the magnetic anisotropy of the adjacent picoline ring [14], it is most reasonable to conclude that the resonances at 6.33 and ca. 7.3 ppm should be ascribed to 6-H and 3-H, respectively.

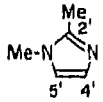
TABLE 2

$^{13}C\{^{1}H\}$ NMR DATA OF IV AND ITS RELATED COMPOUNDS [a]

Compound	Phenylene or Phenyl						Thiazolyl or Imidazoyl		
	1-C	2-C	3-C	4-, 5- and 6-C'S			2'-C	4'-C	5'-C
IV [X = S, Y = $PdCl(PPh_3)$]	151.8 [b]	129.8 [b]	129.0 [c]	124.5 [d],	124.1 [d],	142.0 [d]	178.0 [b]	138.7 [c]	115.1 [c]
Hphtz (X = S, Y = H)	128.5	133.3 [b]	128.5	126.2 (4-C)	129.6 (5-C)	126.2 (6-C)	167.8 [b]	143.3	118.4
Thiazole [e,f]	—	—	—	—	—	—	152.7	143.2	118.6
VIII [X = NEt, Y = $PdCl(PPh_3)$] [g]	152.5 [h]	137.7 [b]	126.5 [d]	121.7 [d],	123.9 [d],	132.2 [d]	151.4 [b]	139.6 [c]	119.2
1,2-Dimethylimidazole [e,h]	—	—	—	—	—	—	144.4 [b]	126.4	120.0







[a] δ(C) (ppm) from TMS, in $CDCl_3$. [b] Quaternary carbon. [c] Doublet due to coupling with ^{31}P. [d] Complete assignment not possible. [e] Numberings 2', 4', and 5' are used for comparison in place of 2, 4, and 5, respectively. [f] Ref. 11. [g] Ref. 5. [h] Ref. 12.

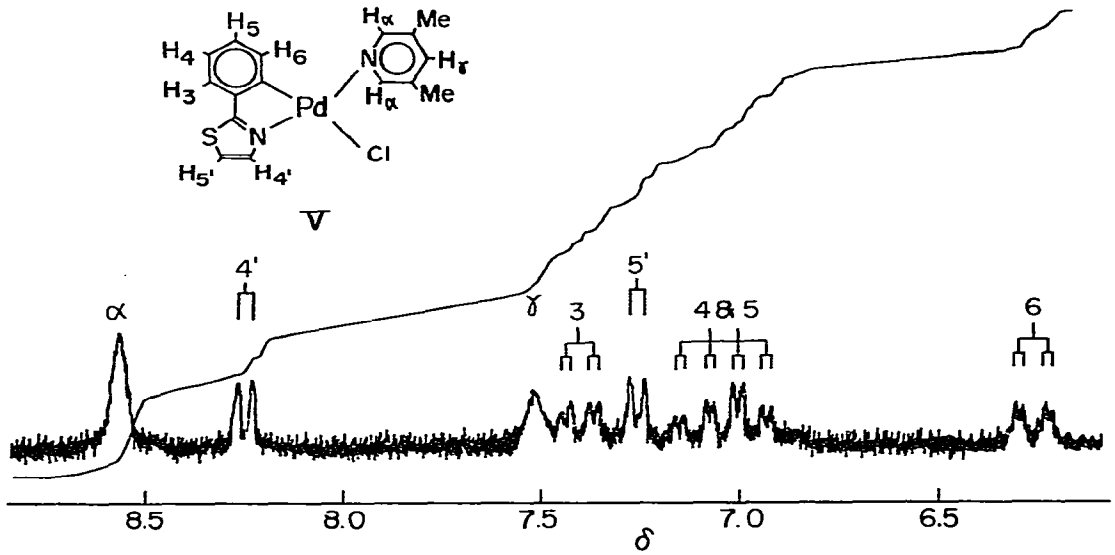


Fig. 1. The ^{1}H NMR spectrum of V in CD_2Cl_2 (δ value in ppm from internal TMS).

ligand. In the ^{1}H NMR spectrum of VI, methyl protons of the acac ligand appeared as two singlets at δ 2.08 (3 H) and 2.02 ppm (3 H). *o*-Phenylene protons of the phtz moiety were observed as complicated multiplets (4 H) in the range of δ 7.0—7.7 ppm. The pattern of the multiplets and their proton number were different from those of Hphtz itself, supporting the cyclopalladated structure in VI.

The reactions of III with vinyl compounds were examined in the presence of excess triethylamine. Complex III reacted with methyl vinyl ketone in refluxing toluene to afford an orange oil, which unexpectedly proved to be Hphtz on the basis of the identity of its ^{1}H NMR and mass spectra with those of an authentic sample. It is noteworthy that no vinylated compounds was isolated in this reaction, in sharp contrast with the results reported previously [15—18]. Another vinylic compound, styrene, did not react with III in refluxing toluene, but did so in refluxing *m*-xylene to give an orange oil. After column chromatographic treatment on silica gel, this oil turned out to contain both Hphtz and *trans*-2-(2′-thiazolyl)stilbene (VII). The ^{1}H NMR spectrum of VII in CCl_4 showed an AB quartet due to two olefinic protons of the styryl moiety at δ 6.86 ($\Delta\delta$ = 0.36, $^3J_{HH}$ = 16 Hz). Such a large coupling constant indicates that the two olefinic protons are situated mutually in *trans* positions. A singlet resonance at δ 7.52 ppm was assigned to two olefinic protons of thiazolyl group, accidentally overlapping to each other. The mechanism yielding Hphtz in these two reactions is obscure and remains to be investigated in connection with recent papers [2,3,19].

In conclusion, the cyclopalladated structures of II—VI were confirmed unambiguously not only by the ^{1}H NMR data (especially the phenylene proton resonances of V), the ^{13}C NMR spectrum of IV (the four quaternary carbons), and the elemental analyses, but also by the formation of *trans*-2-(2′-thiazolyl)-

stilbene. This conclusion is also supported by the X-ray analyses of di-μ-acetato-bis(2-*p*-tolylbenzthiazolato-2′-*C*,*N*)dipalladium(II) and its 2-*p*-tolylbenzoxazolato analogue [6], which were obtained under conditions similar to these used in the present study.

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