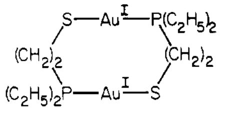
in the last category is found in the gold(I) dimer X.[29] Compound X has been investigated[30] in terms of its being used in arthritis therapy.



X

A logical future extension of this research will involve an exploration of the oxidative addition reactions between thallium(I) dialkyldithiocarbamates and pseudohalogens. The structure of (dipropyldithiocarbamato)thallium(I) dimer has been shown[31] to be different than that of its gold(I) analogue I. It consists of a unique zigzag chain structure in which the distorted $[(C_3H_7)_2NCS_2Tl]_2$ dimers are connected by interdimer Tl-S linkages such that one Tl(I) is six-coordinate while the other is five-coordinate. Instead of an eight-membered ring, it exists as a distorted bipyramid with Tl(I) atoms at the apices.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

Registry No. $[Au(S_2CN(C_2H_5)_2)SCN]_2$, 79255-13-3; $[Au(S_2CN(C_2H_5)_2)_2][Au(SCN)_2]$, 79255-14-4; $[Au(S_2CN(C_2H_5)_2)SeCN]_2$, 79255-15-5; $[Au(S_2CN(C_2H_5)_2)_2][Au(SeCN)_2]$, 79255-17-7; $[Au(S_2CN(C_2H_5)_2)Br]_2$, 79255-18-8; $[Au(S_2CN(C_2H_5)_2)_2][AuBr_2]$, 33916-73-3; $[Au(S_2CN(C_2H_5)_2)I]_2$, 79255-19-9; $[Au(S_2CN(C_2H_5)_2)_2][AuI_2]$, 79255-20-2; $[Au(S_2CN(C_2H_5)_2)_2][Au(SCN)_2Br_2]$, 79255-22-4; $[Au(S_2CN(C_4H_9)_2)SCN]_2$, 79255-23-5; $[Au(S_2CN(C_4H_9)_2)_2][Au(SCN)_2]$, 79255-24-6; $[Ag(S_2CN(C_2H_5)_2)]_6$, 59859-16-4; $[Au(S_2CN(C_2H_5)_2)]_2$, 66712-10-5; $[Au(S_2CN(C_4H_9)_2)]_2$, 59306-90-0; $(SCN)_2$, 505-14-6; $(SeCN)_2$, 27151-67-3; Br_2, 7726-95-6; I_2, 7553-56-2.

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Preparation and Characterization of Novel Six-Membered Cyclopalladated Complexes of 2-Benzylpyridine

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Received March 4, 1981

The novel six-membered cyclopalladated complex bis(μ-acetato)-bis[2-(2-picolyl)phenyl-C^1,*N*]dipalladium(II) {[Pd(OAc)(piph)]$_2$} has been synthesized by the reaction between palladium(II) acetate and 2-benzylpyridine. Its di-μ-chloro analogue, {[PdCl(piph)]$_2$}, yielded by the metathetical reaction with lithium chloride, undergoes bridge-splitting reactions with 3,5-lutidine and thallium(I) acetylacetonate to afford the corresponding mononuclear cyclopalladated complexes. All the cyclopalladated complexes are characterized by means of elemental analysis and mass, IR, and NMR spectroscopy. The cyclopalladated structure of the piph moiety is also confirmed by the formation of 2-(2-vinylated benzyl)pyridines, which were obtained by the reactions of {[PdCl(piph)]$_2$} with styrene and methyl vinyl ketone.

Introduction

In recent years considerable interest has developed concerning the utilization of cyclometalated complexes for organic syntheses.[1,2] Many articles have already been published concerning five-membered cyclometalated complexes having nitrogen, phosphorus, oxygen or sulfur donor atoms.[3-5] However, six-membered cyclometalated complexes are less popular, and only five reports have appeared about six-membered cyclometalation of 2,2′-bis(diphenylphosphino)dibenzyl,[6] *trans*-2,2′-bis(diarylphosphino)stilbene,[7] (*o*-alkoxyphenyl)diorganophosphine,[8] *N*-arylamides,[9,10] and *N*,*N*′-diarylamidines.[9] Moreover, it has been reported that hydrometalation of diphenyl(*o*-styryl)phosphine,[11] oxymetalation of (but-3-enyl)diphenylphosphine,[12] diphenyl(*o*-styryl)phosphine,[13] and dimethyl(*o*-styryl)arsine,[13] and bromometalation of (*o*-allylphenyl)diphenylphosphine[14] also resulted in the formation of six-membered C,P- or C,As-chelating complexes.

In the course of investigation about new cyclopalladation reactions,[15-17] we have found that 2-benzylpyridine (Hpiph) easily reacted with palladium(II) acetate to yield a novel six-membered cyclopalladated complex {[Pd(OAc)(piph)]$_2$}

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Table I. Yields and Analytical Data of the New Complexes

no.	complex	% yield	mp,[a] °C	% found			% calcd		
				C	H	N	C	H	N
1	$[PdCl_2(Hpiph)_2]$	95	222	55.4	4.3	5.4	55.9	4.3	5.4
2	$[PdBr_2(Hpiph)_2]$	77	230	47.3	3.7	4.5	47.7	3.7	4.6
3	$\{[Pd(OAc)(piph)]_2\}$	56	268	49.8	4.0	4.0	50.4	3.9	4.2
4	$\{[PdCl(piph)]_2\}$	90	248	45.5	3.3	4.2	46.5	3.3	4.5
5	$[PdCl(piph)(lut)]\cdot 0.2CH_2Cl_2$	72	257	53.6	4.7	6.4	53.1	4.5	6.5
6	$[Pd(piph)(acac)]$	47	222	54.5	4.7	3.7	54.6	4.6	3.8

[a] All melting points are uncorrected; decomposition occurred in all cases.

(**3**) [piph = 2-(2-picolyl)phenyl-C^1,N]. The present paper deals with this complex and also with the related cyclopalladated complexes derived from **3**.

Experimental Section

The general procedures and spectroscopic techniques were the same as those described in the recent paper from this laboratory.[15] The ^{13}C NMR spectrum was recorded on a JEOL model JNM-FX 90Q spectrometer, with tetramethylsilane as an internal standard. Thallium(I) acetylacetonate [Tl(acac)] was prepared according to the literature.[18] The other reagents were commercial samples and were used without further purification. Yields and analytical data of all the complexes obtained in this study are listed in Table I.

Preparation of $[PdCl_2(Hpiph)_2]$ (1). A methanol suspension (20 mL) containing palladium(II) chloride (1.7 mmol) and Hpiph (3.4 mmol) was refluxed for 2 h. The resulting yellow solid was filtered off and then recrystallized from dichloromethane and hexane to give **1** as a lemon yellow crystal.

Halogen Metathesis of 1. A mixture of **1** (0.58 mmol) and lithium bromide monohydrate (11.6 mmol) was refluxed in acetone (30 mL) for 15 h, and the solvent was evaporated in vacuo. The residue was washed with a methanol/water (1/1) mixed solvent and recrystallized twice from dichloromethane and hexane to give the corresponding bromo complex, $[PdBr_2(Hpiph)_2]$ (**2**), as a yellow crystal.

Preparation of $\{[Pd(OAc)(piph)]_2\}$ (3). An acetic acid (20 mL) suspension containing palladium(II) acetate (1.3 mmol) and Hpiph (1.3 mmol) was refluxed for 1.5 h and then filtered. Water (150 mL) was added to the yellow filtrate, and the mixture was left standing overnight. Precipitated solid was filtered and then recrystallized from dichloromethane and hexane to yield **3** as a pale greenish yellow crystal.

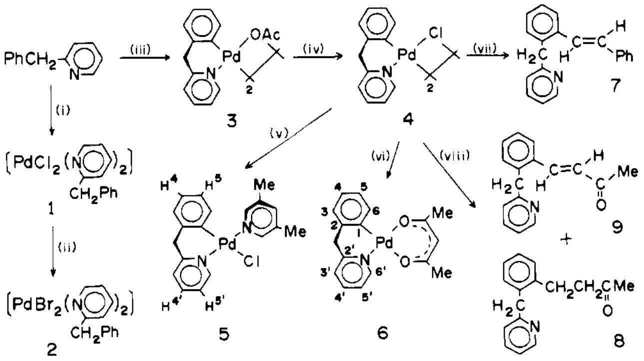
Preparation of $\{[PdCl(piph)]_2\}$ (4). Lithium chloride (1.8 mmol) in water (10 mL) was added to an acetone (20 mL) suspension of **3** (0.45 mmol), and the resulting mixture was stirred for 2 days at room temperature. After filtration, the filtered residue was washed well with a methanol/water (1/1) mixed solvent, to yield **4** as a pale yellow solid.

Reaction of 4 with 3,5-Lutidine (lut). 3,5-Lutidine (0.53 mmol) was added to a dichloromethane (15 mL) suspension of **4** (0.24 mmol). A clear solution formed immediately, which was concentrated after stirring for 5 h at room temperature. Addition of diethyl ether gave $[PdCl(piph)(lut)]\cdot 0.2CH_2Cl_2$ (**5**) as a white crystal.

Reaction of 4 with Tl(acac). Thallium(I) acetylacetonate (0.98 mmol) was added to a suspension of **4** (0.48 mmol) in dichloromethane (15 mL), and the mixture was stirred for 19 h at room temperature. After the resulting milky suspension was centrifuged, the supernatant solution was passed through a silica gel column (200 mesh, 15 mm i.d. × 100 mm) with dichloromethane. A pale yellow fraction was collected and concentrated. Addition of diethyl ether gave [Pd(piph)(acac)] (**6**) as ivory plates.

Reaction of 4 with Styrene. A *m*-xylene (10 mL) suspension containing **4** (0.69 mmol), styrene (3.5 mmol), and triethylamine (2.8 mmol) was refluxed for 5 h. After filtration, the filtrate was evacuated under reduced pressure to yield a greenish yellow oil, which was chromatographed on an activated alumina column (300 mesh, 12 mm i.d. × 135 mm). A pale yellow fraction was eluted by benzene/hexane (2/1) and evaporated to dryness. The residue was recrystallized from pentane to yield *trans*-2-(2-picolyl)stilbene (**7**) as ivory granules: yield 44% (based on **4**), mp 37 °C. ^1H NMR (CCl_4): δ 4.24 s (2 H), 7.11 q [$\Delta\delta$ = 0.59, ^3J(HH) = 16.5 Hz], 6.80–7.65 m (12 H), 8.44 d [^3J(HH) = 6 Hz, 1 H]. IR (KBr): 1640 w, 960 s (*trans*-CH=CH). Anal. Calcd for $C_{20}H_{17}N$: C, 88.52; H, 6.31; N, 5.16. Found: C, 88.68; H, 6.33; N, 5.19. Mass spectrum: *m/e* 271 (P^+).

Scheme I. Preparation of Complexes[a]



[a] Key: (i) $PdCl_2$ in MeOH; (ii) $LiBr\cdot H_2O$ in acetone; (iii) $Pd(OAc)_2$ in AcOH; (iv) LiCl in acetone/water; (v) lut in CH_2Cl_2; (vi) Tl(acac) in CH_2Cl_2; (vii) styrene in *m*-xylene; (viii) methyl vinyl ketone in benzene.

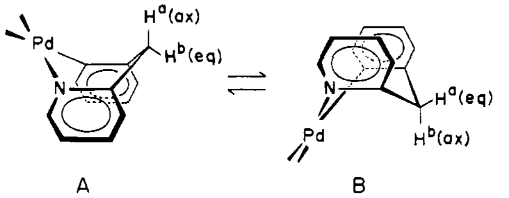


Figure 1. Inversion of the six-membered piph ring.

Reaction of 4 with Methyl Vinyl Ketone. This reaction was carried out in the same way as described above, except that benzene was the solvent. The resulting reddish brown oil (380 mg) was twice chromatographed on an activated alumina column (300 mesh, 12 mm i.d. × 85 mm). Pale yellow and orange-red fractions were obtained by eluting with benzene and benzene/diethyl ether (1/1), respectively. On evaporation of the solvent from the former fraction, methyl 2-(2-picolyl)phenethyl ketone (**8**) was obtained; yield 8% (based on **4**). ^1H NMR ($CDCl_3$): δ 2.01 s (3 H), 2.5–3.0 (AA′BB′ multiplet, 4 H), 4.13 s (2 H), 6.9–7.7 m (7 H), 8.28 d [^3J(HH) = 6 Hz, 1 H]. Mass spectrum: *m/e* 239 (P^+), 196 [$(P - COCH_3)^+$], 168 [$(P - CH_2CH_2COCH_3)^+$].

The latter fraction was also evaporated to dryness to give *trans*-1-(2-(2-picolyl)benzylidene)acetone (**9**) as an oily product, but this oil was contaminated with a very small amount of **8**; yield 13%. ^1H NMR ($CDCl_3$): δ 2.26 s (3 H), 4.30 s (2 H), 7.16 q [$\Delta\delta$ = 1.42, ^3J(HH) = 16 Hz, 2 H], 7.0–7.9 m (7 H), 8.35 d [^3J(HH) = 6 Hz, 1 H]. Mass spectrum: *m/e* 237 (P^+) 194 [$(P - COCH_3)^+$], 168 [$(P - CH{=}CHCOCH_3)^+$].

Results and Discussion

Preparation and General Properties of Complexes. The reaction of palladium(II) chloride with a twofold excess of Hpiph in refluxing methanol yielded only an addition product, dichlorobis(2-benzylpyridine-*N*)palladium(II) $[PdCl_2(Hpiph)_2]$ (**1**). However, the reaction of equimolar amounts of palladium(II) acetate and Hpiph in refluxing acetic acid produced a novel six-membered cyclopalladated complex, {[Pd(OAc)-

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Table II. ^{1}H NMR Spectra[a] of the Palladium(II) Complexes

		Hpiph- or piph-CH_2			δ	
complex	T_m/°C[b]	δ	Δδ	T_c/°C[c]	pyridyl-H$^{6'}$	others[d]
1	5	5.20 s		50	8.74 d[e]	6.74 d[e] (H$^{3'}$), 7.46 t[e,g,h]
		5.35 s			8.89 d[e]	6.82 d[e] (H$^{3'}$)
2	26	5.24 s[f]			8.87 d[e,f]	6.83 d[e] (H$^{3'}$),[f] 7.52 t[e,g,h]
		5.39 s[f]			9.04 d[e,f]	6.91 d[e] (H$^{3'}$)[f]
3[i]	−50	3.15 q[j]	0.51	0	8.56 d[e,k]	1.94 s (OAc-Me)
		4.17 q[j]	0.66			1.97 s (OAc-Me)
5	−35	4.45 q[j]	0.93	10	9.17 dd[e,k,l]	2.29 s (lut-Me), 5.29 s (CH_2Cl_2), 7.46 s (lut-H$^\gamma$), 8.39 s (lut-H$^\alpha$)
6	10	4.41 s		−35	8.93 d[e]	2.08 s (acac-Me), 7.28 t[e,m]
						2.12 s (acac-Me), 7.51 t[e,m]
						5.52 s (acac-CH), 7.54 t[e,m]
						7.79 t[e,h,m]

[a] Measured in $CDCl_3$ except for 3. Abbreviations used: s = singlet, d = doublet, dd = double doublet, q = an AB quartet. [b] Measured temperature. [c] Coalescence temperature. [d] Assignment is given in parentheses, except for triplets. [e] ^3J(HH) = ca. 6 Hz. [f] With intensity ratio of 45:55. [g] H$^{4'}$ or H$^{5'}$ of the pyridyl ring. [h] The other aromatic proton resonances were too complicated to be distinguished. [i] In CD_2Cl_2. [j] $^2J(H_AH_B)$ = 14 Hz. [k] See the text about the other aromatic protons. [l] ^4J(HH) = 1.5 Hz. [m] H^4, H^5, H$^{4'}$, or H$^{5'}$ of the piph moiety.

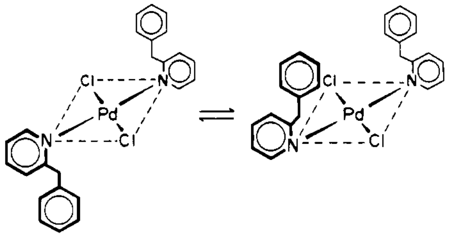

Figure 2. Conformational isomers of 1.

(piph)]$_2$} (3) [piph = 2-(2-picolyl)phenyl-C^1,N]. When this reaction was carried out in refluxing methanol, only palladium black was produced without formation of a noticeable amount of 3. Complex 3 was converted to the chloro-bridged analogue, {[PdCl(piph)]$_2$} (4), by the reaction with excess lithium chloride. Compound 4 was treated with 3,5-lutidine (lut) and Tl(acac) to afford corresponding mononuclear cyclopalladated complexes, [PdCl(piph)(lut)]·0.2CH_2Cl_2 (5) and [Pd(piph)(acac)] (6), respectively (Scheme I). The new cyclopalladated complexes are stable in air and water.

The IR spectra of 1–6 exhibit a band at ca. 1610 cm^{-1} due to the skeletal vibration of the pyridine ring in the Hpiph or piph moiety. A molecular model of the cyclopalladated piph moiety indicates that the six-membered ring has a boat form, as shown in Figure 1. A similar boat-form six-membered structure was found in a pyridyl-bridged binuclear palladium(II) complex, {[PdBr(μ-C_5H_4N-C^2,N)(PPh_3)]$_2$}.[19] The piph–Pd(II) complexes, 3, 5, and 6, show temperature-dependent ^{1}H NMR spectra attributable to the inversion of the six-membered boat-form ring between conformations A and B (Figure 1). The low-temperature limiting spectra were obtained as for 3 and 5 and are summarized in Table II. The inversion of the six-membered boat-form ring may be comparable with that of a six-membered boat-form M–$(NN)_2$–B ring in poly(1-pyrazolyl)borato complexes.[20,21]

Addition Complexes 1 and 2. Complex 1 showed temperature-dependent ^{1}H NMR spectra attributable to an equilibrium between two conformational isomers, as shown in Figure 2. At 5 °C, methylene proton resonances appeared as two singlets with nearly equal intensities at δ 5.20 and 5.35, which turned to one fairly sharp singlet (δ 5.43) at 60 °C. Similarly, two 6′-H's in 1 were observed as two doublets at 5 °C and changed to one broad signal (δ 9.05) at 60 °C. The presence of these two conformational isomers is associated with the quenching of the rotation of two bulky Hpiph ligands around the Pd–N bond. The far-IR spectrum of 1 exhibited two ν(Pd–Cl) frequencies at 344 and 352 cm^{-1}, supporting the two conformational isomers rather than two geometrical isomers.

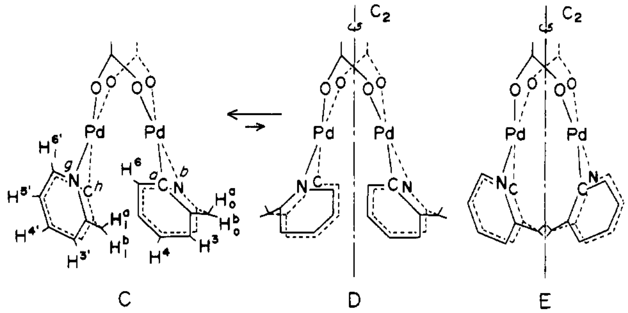

Figure 3. Possible conformations for 3. Methylene protons and H$^{6'}$ of the piph moiety, whose methylene group is situated inside or outside the dihedral angle are represented by the suffixes "i" or "o", respectively.

In the case of 2, the rotation of Hpiph ligands was restricted more strongly by the larger bromo anion, and 2 showed a low-temperature limiting ^{1}H NMR spectrum at 26 °C (Table II).

Acetate-Bridged Dimer 3. The IR spectrum of this complex showed characteristic bands due to bridging acetato ligand at 1585 and 1420 cm^{-1}.[22] In the ^{1}H NMR spectrum at 40 °C, methyl protons of the μ-acetato groups appeared as one sharp singlet at δ 1.99, indicating that 3 has only an (a-C^1, b-N)-(g-N, h-C^1)-type configuration and contains no (a-C^1, b-N)-(g-C^1, h-N)-type one (Figure 3).[15] In consideration of the fact that two coordination planes in an acetato-bridged cyclopalladated dimer are combined by two mutually cis μ-acetato ligands with about 24° of dihedral angle,[23] 3 was expected to have three conformations, C, D, and E, as shown in Figure 3 low temperature. However, the conformations D and E are less favorable, because molecular models indicate that the phenylene and pyridyl protons in conformation D are located very close to each other and that two methylene groups in conformation E collide with each other.

In the ^{1}H NMR spectrum at −50 °C, the acetato methyl protons appeared as two singlets at δ 1.94 (3 H) and 1.97 (3 H). The nonequivalency of the two acetato ligands in conformation C arise undoubtedly both from the absence of such

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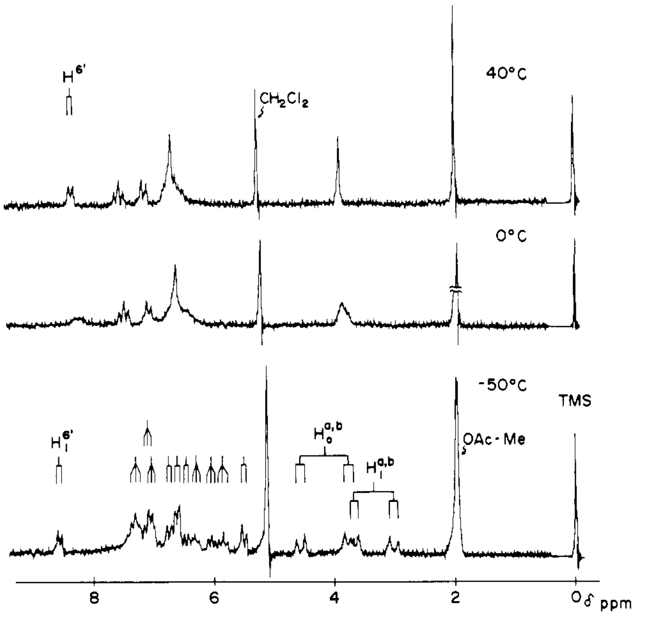

Figure 4. Temperature-dependent ^1H NMR spectra of **3**.

a C_2 axis as is present in conformation D or E and from two different C–O bond lengths in the acetato ligand.[23] The two different C–O bond lengths probably come from the difference between trans influence of the phenylene and pyridyl group. The two mutually nonequivalent methylene groups of the piph moieties were observed as two AB quartets at δ 3.15 and 4.17 (Table II). The upper field signals at δ 3.15 were assigned to H_i^a and H_i^b (see Figure 3C) on the basis of magnetic anisotropy due both to the phenylene ring and to the pyridyl ring of the other piph moiety. As for aromatic protons, the ^1H NMR spectrum at −50 °C contained four doublets [δ 5.51 (1 H), 6.47 (1 H), 6.62 (2 H) and 6.76 (1 H); $^3J(HH)$ = ca. 7 Hz] and six triplets [δ 5.86 (1 H), 6.04 (1 H), 6.32 (1 H), 7.04 (1 H), 7.08 (1 H), and 7.32 (2 H); $^3J(HH)$ = ca. 7 Hz] (Figure 4).[24] The former seven signals, corresponding to eight protons, were observed at rather high fields, possibly owing to the anisotropic shielding by the phenylene or pyridine ring. A doublet at δ 8.56 (1 H) was ascribed to $H_i^{6'}$ of one of the pyridyl groups. These data indicate that the inversion of the six-membered piph ring is quenched virtually at −50 °C and that **3** has conformation C.

Upon warming of the sample from −50 °C, the two AB-type quartets due to the methylene groups and the two acetato methyl resonances broadened gradually and coalesced at 0 °C (Figure 4). At 40 °C, the methylene protons changed to a considerably sharp singlet at δ 3.92, analogous to the acetato methyl resonance. At the same temperature, aromatic proton resonances appeared as two doublets at δ 7.11 [$^3J(HH)$ = 7 Hz, 2 H; H^3, H^6, or $H^{3'}$] and 8.36 [$^3J(HH)$ = 6 Hz, 2 H; $H^{6'}$], one triplet at δ 7.55 [$^3J(HH)$ = 7 Hz, 2H; H^4, H^5, $H^{4'}$, or $H^{5'}$], and complicated signals in the range of δ 6.4–6.9 (10 H). These facts imply that the inversion of the six-membered ring took place rapidly on the NMR time scale, forming the quasi-stable conformation D during a limited time.

Chloro-Bridged Dimer 4. The characteristic IR bands of the bridging acetato ligands, observed in **3**, disappeared. Though the ^1H NMR spectrum of **4** could not be obtained owing to its insolubility in common organic solvents, **4** was assigned to the chloro-bridged analogue of **3**, {[PdCl(piph)]$_2$}, in view of the fact that **4** easily underwent both typical bridge-splitting reactions to yield corresponding mononuclear cyclopalladated complexes, as seen just later, and vinylation reactions to give 2-(2-vinylated benzyl)pyridines.

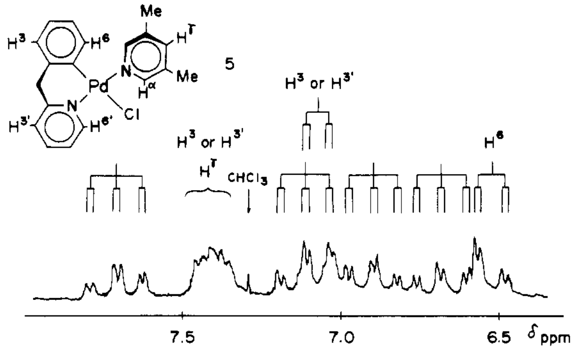

Figure 5. Low-field region of the ^1H NMR spectrum of **5** at −35 °C.

Mononuclear Complex of [PdCl(piph)(lut)]·0.2CH$_2$Cl$_2$ (5). The IR spectrum of **5** exhibited a very similar pattern to that of **4**. Complex **5** also showed a stereochemical nonrigid property attributable to the inversion of the six-membered piph moiety above −30 °C. In the low-temperature limiting spectrum at −35 °C, the methylene protons of the piph moiety were observed at δ 4.45 as an AB quartet, which changed to a sharp singlet at δ 4.51 in the high-temperature limiting spectrum at 55 °C.

As for the aromatic protons of **5** measured at −35 °C, the eight protons of the piph moiety appeared as two sets of ABCD patterns, together with two singlets due to H^α and H^γ of the lut moiety at δ 8.39 and ca. 7.4, respectively (see Figure 5). A double doublet at δ 6.56 (1 H) was assigned to H^6 of the *o*-phenylene moiety, in consideration of the magnetic anisotropy of the adjacent lutidine ring.[17,25] By contrast, the $H^{6'}$ of the pyridyl group appeared as a double doublet at the lowest field (δ 9.17, 1 H). Two other double doublets at δ 7.07 (1 H) and ca. 7.4 (1 H) were ascribed to H^3 and $H^{3'}$ protons. Four double triplets assignable to H^4, H^5, $H^{4'}$, and $H^{5'}$ appeared at δ 6.72 (1 H), 6.92 (1 H), 7.10 (1 H) and 7.64 (1 H). The coupling constants were $^3J(HH)$ = 7.5 Hz and $^4J(HH)$ = 1.5 Hz. These results indicate unambiguously the cyclopalladated structure of the piph moiety in **5**.

Mononuclear Complex of [Pd(piph)(acac)] (6). The IR spectrum of **6** showed characteristic bands due to an O,O′-chelating acetylacetonato group at 1515 and 1580 cm^{-1}. The mass spectrometry gave the parent peak at *m/e* 373 corresponding to ^{106}Pd and the fragment peak at *m/e* 274 [(P − acac)$^+$]. These results also support the presence of the cyclopalladated structure of piph in **6**.

Complex **6** showed its high-temperature limiting ^1H NMR spectrum at 10 °C (Table II), exhibiting a sharp singlet due to the methylene protons of the piph moiety at δ 4.41. The singlet began to broaden near −20 °C, reached the coalescence point at −35 °C, and changed into two very broad humps near δ 4.0 and 4.6 at −50 °C. The low-temperature limiting spectrum could not be obtained, because the NMR sample solution began to freeze below −50 °C.

The ^1H-decoupled ^{13}C NMR spectrum of **6** in CDCl$_3$ exhibited three aromatic quaternary carbon signals of the piph moiety. A singlet at δ 160.0 was assigned to 2′-C, referring to the 2-carbon resonance of 2-ethylpyridine (δ 163.4, in CDCl$_3$).[26] The other two quaternary carbons of 1-C and 2-C were observed as singlets at δ 143.3 and 136.5. These data also confirm strongly the cyclopalladated structure of the piph moiety in **6**. Eight other aromatic tertiary carbon resonances appeared at δ 152.2, 138.0, 133.9, 125.3, 125.0, 124.2, 124.0,

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(24) The remaining three proton resonances could not be distinguished owing to overlapping with the above-mentioned signals.

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and 122.0 as singlets. Only the first signal at δ 152.2 was assigned to 6′-C by referring to 2-ethylpyridine (6-C, δ 149.1).[26] The methylene carbon of the piph moiety was observed at δ 48.9 as a singlet. Five carbons of the acac ligand appeared as singlets at δ 187.9 (C=O), 186.8 (C=O), 100.2 (CH), 28.2 (CH_3), and 27.7 (CH_3).

Reactions of 4 with Vinyl Compounds. The reactions of **4** with styrene and methyl vinyl ketone were examined in the presence of triethylamine.[2,27,28] Complex **4** reacted with styrene in refluxing *m*-xylene to yield *trans*-2-(2-picolyl)stilbene (**7**) in 44% yield. The IR, ^{1}H NMR, and mass spectra of **7** were in accord with the proposed formula.

Methyl vinyl ketone also reacted with **4** under milder conditions (in refluxing benzene) to afford a reddish brown oil. Its ^{1}H NMR spectrum indicated that the oil contained about 81% of *trans*-1-(2-(2-picolyl)benzylidene)acetone (**9**), about 8% of methyl 2-(2-picolyl)phenethyl ketone (**8**), and an unknown product and that the yield of **9** corresponded to nearly 80%. The ^{1}H NMR spectrum of **9** exhibited typical trans-vinylene protons as an AB quartet at δ 7.16 [$\Delta\delta = 1.42$, $^{3}J(\mathrm{HH}) = 16$ Hz], whereas that of **8** showed an AA′BB′ pattern assignable to the ethylene group in the range of δ 2.5–3.0 (4 H) in place of the trans-vinylene protons. Even after the repeated column chromatographic treatments on alumina, **9** could not be isolated in a pure state owing to the contamination with a small amount of **8**. The formations of **7** and **9** strongly confirm the cyclopalladated structure of the piph moiety. The mechanism to form **8** is not clear at the present time, but the detail will be reported in a following paper.

Concluding Remarks.

The novel six-membered piph cyclopalladated structure in **3**–**6** was unambiguously confirmed on the basis of their elemental analyses, the aromatic proton resonances in the ^{1}H NMR spectra of **5**, the three quaternary carbons in the ^{13}C{^{1}H} NMR spectrum of **6**, and the formation of 2-(2-vinylated benzyl)pyridines. It is noteworthy that 2-benzylpyridine reacted smoothly with palladium(II) acetate to give the novel six-membered cyclopalladated complex **3**, in sharp contrast with the reaction with palladium(II) chloride leading to the formation of the addition product **1**. It has been already reported that palladium(II) acetate reacts to give five-membered cyclopalladation products with aryl-substituted nitrogen bases[15,17,22,23] and benzyl sulfide,[16] which afforded no cyclopalladated complex by the reactions with pallaldium(II) chloride or tetrachloropalladate(II) ion.

Acknowledgment. We thank Mrs. Hisako Mazume and Miss Yumi Kojima, Nagasaki University, for their technical assistance.

Registry No. **1**, 79272-87-0; **2**, 79272-88-1; **3**, 79272-89-2; **4**, 79299-89-1; **5**, 79272-90-5; **6**, 79272-91-6; **7**, 79272-71-2; **8**, 79272-72-3; **9**, 79272-73-4; methyl vinyl ketone, 78-94-4; styrene, 100-42-5.

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Reactivity of Lanthanide Metal Vapor with Unsaturated Hydrocarbons. Reactions with Ethene, Propene, and 1,2-Propadiene[1]

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Received April 28, 1981

The reactions of ytterbium, samarium, and erbium metal vapor with ethene, propene, and 1,2-propadiene have been investigated by cocondensation of the metals with these hydrocarbons at 77 K followed by isolation and physical and chemical characterization of the organolanthanide products at room temperature. A variety of reaction pathways are traversed in these systems. Evidence for lanthanide metal insertion into C–H bonds, cleavage of carbon–carbon multiple bonds, homologation, oligomerization, and dehydrogenation is observed with these small hydrocarbon substrates. Cyclopropane is similarly highly reactive with erbium metal vapor.

Introduction

During the past few years, we have been investigating[3–7] the low-valent chemistry of the lanthanide elements in efforts to demonstrate experimentally that these metals have a more extensive chemistry than is found in their traditional, ionic, trivalent complexes and to provide a basis for seeking unusual catalytic transformations which involve the 4f elements. One approach which we have used in this study is the metal vaporization technique[8–13] in which metal vapor and a substrate are cocondensed at low temperature. This method has allowed us to examine the reactivity of zerovalent lanthanide metals

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