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Journal of Organometallic Chemistry 547 (1997) 199–207

Journal of Organometallic Chemistry

Bicyclic cyclopalladated complexes derived from *N*-benzyl-substituted Schiff's bases

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Received 29 September 1996; received in revised form 20 June 1997

Abstract

2-Benzylamino-2-penten-4-one (Hacac-bn) reacts with $Pd(MeCO_2)_2$ and $[Pd(MeCO_2)_2(SPr^i_2)_2]$ in benzene at 50°C to give an *N,O*-chelated complex, $[Pd(acac\text{-}bn)_2]$ and a bicyclic cyclopalladated complex, $[Pd(acac\text{-}NCH_2C_6H_4)(SPr^i_2)]$, respectively. Diisopropyl sulfide ligand in the latter complex is replaced easily by PPh_3, giving $[Pd(acac\text{-}NCH_2C_6H_4)(PPh_3)]$. *N*-(Salicylidene)benzylamine (Hsal-bn) also reacts similarly with $Pd(MeCO_2)_2$ and $[Pd(MeCO_2)_2(SPr^i_2)_2]$ at 50°C to afford $[Pd(sal\text{-}bn)_2]$ and $[Pd(sal\text{-}NCH_2C_6H_4)(SPr^i_2)]$, respectively. *N*-(3,5-Dichlorosalicylidene)benzylamine (Hdcsal-bn) reacts with $[Pd(MeCO_2)_2(SPr^i_2)_2]$ and $Pd(MeCO_2)_2$ in the presence of $PPh_2(OMe)$ at 50°C to yield cyclopalladated complexes, $[Pd(dcsal\text{-}NCH_2C_6H_4)(SPr^i_2)]$ and $[Pd(dcsal\text{-}NCH_2C_6H_4)\{PPh_2(OMe)\}]$, respectively. $[Pd(MeCO_2)_2(dmpy)_2]$ (dmpy = 3,5-dimethylpyridine) reacted with Hdcsal-bn in 1:1 and 1:2 molar ratios at 50°C to give $[Pd(dcsal\text{-}bn)(MeCO_2)(dmpy)]$ and $[Pd(dcsal\text{-}bn)_2]$, respectively. The functions of SPr^i_2 and dmpy in these reactions are discussed. © 1997 Elsevier Science S.A.

1. Introduction

Cyclometallation is the direct conversion of carbon–hydrogen bonds of organic bases into carbon–metal bonds with metal compounds [1,2]. Many cyclometallated complexes have a bidendate chelate, involving one carbon atom and a hetero one as coordinating sites. However, a bicyclic cyclometallated complex has a terdentate chelate, which contains one carbon atom and two hetero ones as coordinating sites. Such bicyclic cyclometallated structure is expected to be more rigid and stable than the bidentate-type cyclometallated one. Stable cyclometallated complexes are preferable to practical application, for example, liquid crystals [3].

Masters and Shaw [4] prepared bicyclic cyclometallated complexes derived from 1,3-bis(di-*t*-butylphosphino)pentane. Grove et al. [5] and van der Zeijdeg et al. [6] studied bicyclic cyclometallated complexes derived from 1,3-bis(*N,N*-dimethylaminomethyl)benzene. Several groups reported new types of bicyclic cyclometallated complexes, having terdentate *P,C,P'*-[7,8], *S,C,S'*- [9], *N,C,N'*- [10], *N,N',C*- [11–17], and *O,N,C*-chelates [18–21]. Recently, Perera and Shaw [22] and Perera et al. [23] reported that aryl- or heterocycle-substituted azinephosphines formed novel *P,N,C*-type bicyclic cyclometallated complexes.

There have been several reports on bidentate-type cyclopalladation of *N*-benzylidene-amines [24–26] and benzylamine derivatives [26–28]. However, there are few reports on the bicyclic cyclopalladated complex derived from benzyl-substituted Schiff's base. Here, we will deal with *O,N,C*-type bicyclic cyclopalladation of *N*-benzyl-substituted Schiff's bases derived from acetylacetone and salicylaldehydes.

2. Experimental

All manipulations, elemental analyses, and spectroscopic measurements of the complexes were carried out according to similar manners described in the previous paper [29]. IR spectra of the resulting complexes were analyzed referring the literature [30].

Diacetatobis(diisopropyl sulfide)palladium(II) $[Pd(MeCO_2)_2(SPr^i_2)_2]$ (**1**) [31,32], 2-benzylamino-2-pentene-4-one (Hacac-bn) [33], and *N*-(salicylidene)- and *N*-(3,5-dichlorosalicylidene)-benzylamines [34]

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PII S0022-328X(97)00377-X

(Hsal-bn and Hdcsal-bn, respectively) were prepared by means of the literature. The other reagents were purchased and used without further purification. All the solvents were dried and distilled under nitrogen before use.

2.1. Diacetatobis(3,5-dimethylpyridine)palladium(II) 2

A benzene solution containing $Pd(MeCO_2)_2$ (2.0 mmol) and 3,5-dimethylpyridine (dmpy, 4.0 mmol) was heated at 70°C for 26 h. The reaction mixture was filtered to remove reduced palladium. The solvent was removed under reduced pressure to give greenish white solids, $[Pd(MeCO_2)_2(dmpy)_2]$ (**2**). Yield 33%. IR (KBr disk), 1640s, 1600m (C=N, C=C), 1570vs, 1415vs (CO_2), 1460m, 1380m, 1300vs (CH_3), 795m, 705vs cm^{-1} (disubstituted pyridine ring). ^1H NMR ($CDCl_3$), 1.85 (s, 6H, CH_3CO_2), 2.30 (s, 12H, CH_3 in dmpy), 7.36 (s, 2H, 4-H), 8.31 (s, 4H, 2,6-H).

2.2. Reactions of Hacac-bn with palladium(II) complexes

2.2.1. Reaction of Hacac-bn with $Pd(MeCO_2)_2$

$Pd(MeCO_2)_2$ (0.32 mmol) was added to a benzene solution (20 cm^3) of Hacac-bn (0.32 mmol). The mixture was stirred at 50°C for 2 h. The reaction mixture was concentrated at a reduced pressure and diluted with hexane to give yellow powders, $[Pd(acac\text{-}bn)_2]$ (**3**). Yield 56% based on Hacac-bn. IR (KBr disk) 1585s, 1510vs (C=O, C=C), 1455m (CH_2, CH_3), 1340s (CH_3), 1240m (C–N), 755s, 725s cm^{-1} (C_6H_5).

2.2.2. Reactions of Hacac-bn with $[Pd(MeCO_2)_2(SPr^i_2)_2]$ 1

A benzene solution (20 cm^3) containing 0.32 mmol of Hacac-bn and 0.32 mmol of **1** was kept at 50°C for 1.5 h. The mixture was dried in vacuo. The residue was crystallized from dichloromethane and hexane to afford yellow–khaki powders, $[Pd(acac\text{-}NCH_2C_6H_4)(SPr^i_2)]$ (**4**). Yield 72%. IR (KBr disk) 1595s, 1520vs (C=O, C=C), 740vs cm^{-1} (*ortho*-C_6H_4).

When Hacac-bn (0.43 mmol) reacted with **1** (0.43 mmol) in benzene (20 cm^3) at 10°C for 1.5 h similarly, the ^1H NMR spectrum of the reaction product indicated that the product consisted of **3** and **4** in a molar ratio of about 3:1.

2.2.3. $[Pd(acac\text{-}NCH_2C_6H_4)(PPh_3)]$

A benzene solution (20 cm^3) of **4** (0.20 mmol) and PPh_3 (0.20 mmol) was warmed at 50°C for 1 h. The reaction mixture was concentrated at a reduced pressure and diluted with hexane. The pale-yellow powders precipitated and were washed with hexane to give $[Pd(acac\text{-}NCH_2C_6H_4)(PPh_3)]$ (**5**). Yield 77%. IR (KBr disk) 1580s, 1510vs (C=O, C=C), 1435vs (P–C), 740s (*ortho*-C_6H_4), 695vs cm^{-1} (C_6H_5). $^{13}C\{^1H\}$ NMR (δ, singlet unless noted elsewhere, $CDCl_3$): 21.2 (CH_3), 25.8 (CH_3), 65.2 (CH_2), 97.9 (CH=), 120.3, 123.1, 124.0 (These three singlets are due to the C_6H_4 group), 127.9 [d, $^3J(CP)$ = 11.7 Hz, *meta-C* of the PPh_3 ligand], 130.3 (*para-C* of the PPh_3), 131.0 [d, $^1J(CP)$ = 47 Hz, *ipso-C* of the PPh_3], 135.6 [d, $^2J(CP)$ = 11.7 Hz, *ortho-C* of the PPh_3], 139.9 [d, $^3J(CP)$ = 11.7 Hz], 146.2 [d, $^2J(CP)$ = 7.8 Hz, Pd–C], 152.5 (CH_2–*C*), 163.7 (CH_3–*C*–N), 177.7 (CH_3C=O).

2.3. Reactions of Hsal-bn and Hdcsal-bn with palladium(II) complexes

2.3.1. Reactions of Hsal-bn with $Pd(MeCO_2)_2$

A benzene solution (20 cm^3) containing both Hsal-bn (0.45 mmol) and $Pd(MeCO_2)_2$ (0.45 mmol) was stirred at room temperature for 1 h. The reaction mixture was dried in vacuo. The residue was recrystallized from dichloromethane and hexane to give orange solids, $[Pd_2(sal\text{-}bn)_2(\mu\text{-}MeCO_2)_2]\cdot CH_2Cl_2$ (**6a**). Yield 34%. IR (KBr disk) 1615vs (C=N), 1560vs, 1420vs (CO_2), 1450s (CH_2, CH_3), 1325s (CH_3), 1150m (C–N), 750vs (*ortho*-C_6H_4), 735m, 695s cm^{-1} (C_6H_5).

When Hsal-bn (0.89 mmol) reacted with $Pd(MeCO_2)_2$ (0.45 mmol) in benzene at 50°C for 1 h, yellow precipitates were formed. After filtration, the precipitates were washed with hexane to give yellow solids, $[Pd(sal\text{-}bn)_2]$ (**7**). Yield 81% based on Hsal-bn. IR (KBr disk) 1615vs (C=N), 1600s (C=C of benzene ring), 1450s (CH_2), 1130m (C–N), 740s (*ortho*-C_6H_4), 760vs, 695s cm^{-1} (C_6H_5).

2.3.2. Reactions of Hsal-bn and Hdcsal-bn with 1 at 50°C

A benzene solution (20 cm^3) containing 0.32 mmol of Hsal-bn and 0.32 mmol of **1** was kept at 50°C for 1.5 h. After filtration, the filtrate was concentrated under a reduced pressure and diluted with hexane to afford khaki–brown powders, $[Pd(sal\text{-}NCH_2C_6H_4)(SPr^i_2)]$ (**8a**). Yield 63%. IR (KBr disk) 1625vs (C=N), 1605s (C=C of benzene ring), 1455m (CH_2, CH_3), 765vs, 740vs, 700s cm^{-1} (*ortho*-C_6H_4).

Similarly, Hdcsal-bn reacted with **1** in benzene at 50°C for 1 h to give orange powders, $[Pd(dcsal\text{-}NCH_2C_6H_4)(SPr^i_2)]$ (**8b**). Yield 64%. IR (KBr disk) 1625vs (C=N), 1580s (C=C of benzene ring), 1460vs (CH_2, CH_3), 1160vs (C–N).

2.3.3. Reaction of 8b with trimethyl phosphite

A benzene solution (15 cm^3) of **8b** (0.20 mmol) and trimethyl phosphite (0.81 mmol) was heated at 50°C for 1 h. After filtration and similar work-up to the case of **8a**, the resulting yellow solids were washed with hexane to give $[Pd(dcsal\text{-}NCH_2C_6H_4)\{P(OMe)_3\}]$ (**9**). Yield 82%. IR, 1620vs (C=N), 1440vs (CH_2, CH_3), 1315s

(CH_3), 1155vs (C–N), 1010vs (P–O–C), 855s, 800vs, 760vs, (tetrasubstituted benzene and *ortho*-C_6H_4). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 85% H_3PO_4) δ 122.0.

2.3.4. Reaction of Hdcsal-bn with $Pd(MeCO_2)_2$ in the presence of methyl diphenylphosphinite

A benzene solution (15 cm^3) containing $Pd(MeCO_2)_2$ (0.67 mmol), Hdcsal-bn (0.69 mmol), and methyl diphenylphosphinite (1.34 mmol) was kept at 50°C for 1 h. After filtration and similar work-up to the case of **8a**, dark orange solids [Pd(dcsal-$NCH_2C_6H_4$){PPh_2(OMe)}] (**10**) were obtained. Yield 16%. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 85% H_3PO_4) δ 32.0.

2.4. Reactions of 2 with Hacac-bn, Hsal-bn and Hdcsal-bn

2.4.1. Reaction of 2 with Hacac-bn

A benzene solution (20 cm^3) containing 0.23 mmol of Hacac-bn and 0.23 mmol of **2** was kept at 50°C for 7 h. The reaction mixture was applied on a silica-gel column. A pale yellow fraction with benzene was evaporated to dryness to give yellow powders **3**. Yield 74% based on Hacac-bn.

2.4.2. Reactions of 2 with Hsal-bn

A benzene solution (20 cm^3) of Hsal-bn (0.46 mmol) and **2** (0.23 mmol) was heated to 50°C, changed gradually to a yellow suspension, and was stirred at this temperature for 27 h. The resulting precipitates were collected and washed with hexane to give yellow powders **7**. Yield 87%.

Similarly, equimolar quantities of **2** and Hsal-bn (each, 0.46 mmol) were treated in 20 cm^3 of benzene at 50°C for 27 h. The resulting yellow precipitates (45 mg) were mainly **7**, which was contaminated with about 13% of **2** (in weight). Khaki solids (20 mg) were recovered from the remaining solution and revealed to be a mixture of **2**, **7** and Hsal-bn in a molar ratio of 10:2.3:2.9 by the ^1H NMR spectrum.

2.4.3. Reactions of 2 with Hdcsal-bn

A benzene solution (20 cm^3) involving 0.23 mmol of Hdcsal-bn and 0.23 mmol of **2** was kept at 50°C for 2 h. The solvent was evaporated to dryness, and the residue was recrystallized from benzene and hexane to afford yellow solids, [Pd(dcsal-bn)($MeCO_2$)(dmpy)] (**11**). Yield 36%. IR (KBr disk) 1635 vs, 1625vs (C=N and CO_2), 1455s (CH_2, CH_3), 1310vs (CO_2), 1180m (C–N), 875m, 775s, 690m cm^{-1} (disubstituted pyridine, 1,2,3,5-tetrasubstituted benzene, C_6H_5).

A benzene solution (20 cm^3) containing **2** (0.23 mmol) and Hdcsal-bn (0.46 mmol) was heated at 50°C for 2 h. Brilliant yellow solids precipitated and were washed with hexane to afford [Pd(dcsal-bn)$_2$] (**12**). Yield 40 mg, 26%. Pale yellow solids (60 mg) were recovered from the remaining solution and characterized to be a mixture of **11**, Hdcsal-bn and **12** in a molar ratio of 10:9.6:1.0 by the ^1H NMR spectrum.

3. Results and discussion

Melting points and elemental analyses of the resulting palladium(II) complexes are summarized in Table 1.

3.1. Reactions of $Pd(MeCO_2)_2$ with the N-benzyl-substituted Schiff's bases

Equimolar quantities of Hacac-bn and $Pd(MeCO_2)_2$ reacted in benzene at 50°C to give the 1:2-type complex, [Pd(acac-bn)$_2$] (**3**) in a moderate yield. The aromatic region of the ^1H NMR spectrum of **3** showed two triplets at δ 7.17 (4H) and 7.29 (2H) and one doublet at δ 7.35 (4H), which were characteristic of a phenyl group (Table 2). These data and the elemental analyses indicate that **3** is a bis(*N,O*-chelate)palladium(II) complex, but not a bicyclic cyclopalladated one (Scheme 1).

Hsal-bn reacted with an equimolar quantity of $Pd(MeCO_2)_2$ at room temperature in benzene to give the orange-colored complex, [Pd_2(sal-bn)$_2$(μ-$MeCO_2$)$_2$]·CH_2Cl_2 (**6a**). The IR spectrum of **6a** exhibited three very strong absorptions at 1615, 1560, and 1420 cm^{-1}, assignable to ν(C=N) and assymetric and symmetric stretching frequencies of CO_2 moiety, respectively. The ^1H NMR spectrum of **6a** showed a singlet at δ 2.01 (6H), ascribable to acetato-methyl protons (Table 3). An AB type quartet at δ 3.86 (2H, ^2J = 14.4 Hz) and 4.72 (2H) were assigned to benzyl-methylene protons, which were located at unequivalent environments. These data indicate unambiguously that **6a** has a bis-μ-acetato-bridged dinuclear structure which contains two Pd(sal-N-*N,O*) planes with a dihedral angle (Scheme 2). The two Pd(sal-N) planes impose re-

Table 1
Melting points and elemental analyses of the palladium complexes

Complex	Melting point (°C)	Analysis[a] (%)		
		C	H	N
2	197–199	49.2 (49.3)	5.4 (5.4)	6.8 (6.4)
3	190–193	59.1 (59.7)	5.8 (5.9)	5.9 (5.8)
4	95–98	52.0 (52.5)	6.4 (6.6)	3.7 (3.4)
5	103–106	65.2 (64.8)	5.3 (5.1)	2.3 (2.5)
6a	222–225	47.0 (47.4)	3.9 (3.9)	3.6 (3.35)
7	271–275	63.6 (63.8)	4.7 (4.6)	5.2 (5.3)
8a	130–134	55.0 (55.4)	5.5 (5.8)	3.4 (3.2)
8b	99–103	47.1 (47.8)	4.5 (4.6)	3.0 (2.8)
9	107–110	40.2 (40.1)	3.6 (3.6)	2.7 (2.75)
10	93–97	53.2 (53.9)	3.9 (3.7)	1.9 (2.3)
11	95–103	50.1 (50.1)	4.4 (4.0)	5.4 (5.1)
12	294	50.6 (50.6)	3.0 (3.0)	4.25 (4.2)

[a] Calculated value is given in the parentheses.

Table 2
^{1}H NMR data[a] of 2-benzylamino-2-pentene-4-one and its palladium complexes

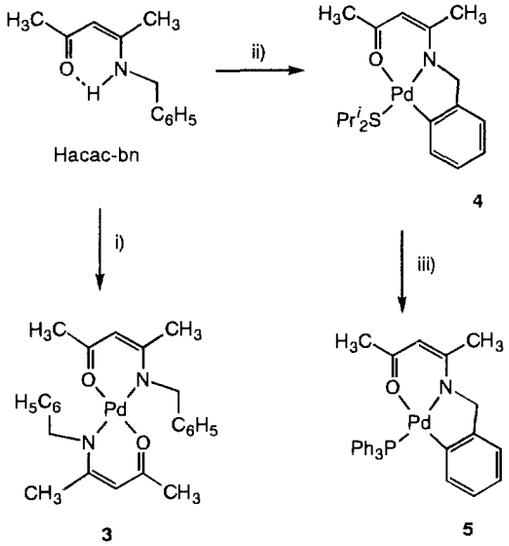
Compound	acac-N moiety		Benzyl moiety		Others
	CH_3	CH	CH_2	Phenyl or *ortho*-phenylene	
Hacac-bn	1.91 (3H) 2.03 (3H)	5.04	4.45 (d, 6.6, 2H)	7.25 (t, 7, 3H, *meta*-H and *para*-H) 7.33 (d, 7, 2H, *ortho*-H)	11.2 (br, NH)
3	1.62 (6H) 1.89 (6H)	4.81 (2H)	4.70 (4H)	7.17 (t, 7.3, 4H, *meta*-H) 7.29 (t, 7.3, 2H, *para*-H) 7.35 (d, 7.3, 4H, *ortho*-H)	–
4	1.93 (3H) 2.08 (3H)	4.95	4.82 (2H)	6.94 (t, 7.6) 7.00 (t, 7.2) 7.07 (d, 7.2) 7.50 (d, 7.6)	1.46 (d, 6.7, 12H, CH_3) 3.54 (sep, 6.7, 2H, CH)
5	1.52 (3H) 2.11 (3H)	4.94	4.95 (2H)	6.42 (t, 7.2) 6.55 (dd, 7.7, 7.0) 6.88 (d, 7.2) 7.11 (d, 7.7)	7.34 (td, 7, 1.3, 6H, *meta*-H of PPH_3) 7.42 (tq, 7, 1.3, 3H, *para*-H of PPh_3) 7.76 (ddd, 8.4, 7, 1.3, 6H, *ortho*-H of PPh_3)

[a]δ value from TMS in $CDCl_3$ at 30°C. Singlet and/or single proton unless noted in the parentheses. Multiplicity, coupling constant (Hz), proton number and assignment of the other signal are presented in the parentheses.

strictions on the rotation of the benzyl groups and make the methylene protons unequivalent. The methine proton resonated at a remarkably high field (δ 6.36) by shielding effect of the salicylidene-phenylene group situated face to face. It is well known that 'Pd(η^3-C_3H_5)($MeCO_2$)' [35], 'PdCl($MeCO_2$)(PMe_2Ph)' [36], and cyclopalladated acetato complexes [37–39] have *cis*-bis(μ-acetato)-bridged dinuclear structures. Particularly, [Pd_2 (C_6H_3Me–$C_7H_4NS)_2$(μ-$CH_3CO_2)_2$] (C_7H_4NS = 2-benzothiazolyl) and its benzoxazolyl analogue have *cis*-bis(μ-acetato)-bridged dinuclear structures with about 24° of dihedral angle [37]. Complex **6a** has no cyclopalladated structure.

When $Pd(MeCO_2)_2$ was treated with 2 times molar amount of Hsal-bn at 50°C, the yellow complex [Pd(sal-bn)$_2$] (**7**) was obtained in a good yield. The ^{1}H NMR spectrum of **7** exhibited a characteristic pattern of the phenyl groups besides four signals for the phenylene group of the salicylidene moiety, implying the lack of the cyclopalladated structure. Previously, the X-ray structure analysis of the related *trans*-bis(*N*-salicylidene-*t*-butylaminato) palladium(II) was reported [40].

Since $Pd(MeCO_2)_2$ has an acetato-bridged trinuclear structure, **6a** is regarded as an intermediate from the trinuclear $Pd(MeCO_2)_2$ to the bis-*N,O*-chelate complex **7**. In fact, **6a** was quantitatively converted into **7** by heating in the presence of Hsal-bn. As for **7** and **3**, which were obtained from $Pd(MeCO_2)_2$, the cyclopalladation of the benzyl group was not detected at all, although $Pd(MeCO_2)_2$ acted as a good metallating reagent for many phenyl or benzyl-substituted Lewis bases, such as *N*-benzylideneaniline [24], 1-ethyl-2-phenylimidazole [41], 2-phenylthiazole [42], 2-benzylpyridine [43], and so on. Since both Hacac-bn and Hsal-bn have a protic hydrogen, anions derived from these Schiff's bases bring about ligand exchange reaction with acetato to form the six-membered *N,O*-chelates. As for the benzyl-substituted Schiff's bases, the bis-*N,O*-chelate complexes were preferentially formed at 50°C owing to high stability of the *N,O*-chelate structure.



Scheme 1. (i) $Pd(MeCO_2)_2$. (ii) [$Pd(MeCO_2)_2(SPr^i_2)_2$] **1**. (iii) PPh_3.

3.2. Reactions of [$Pd(CH_3CO_2)_2(SPr^i_2)_2$] 1 with the N-benzyl-substituted Schiff's bases

Previously, we reported that $Pd(MeCO_2)_2$ reacted with benzene at 70°C in the presence of dialkyl sulfide and metallated benzene directly to give a diphenyltripalladium(II) complex [Pd_3Ph_2(μ-$MeCO_2)_4(SR_2)_2$] [31]. Complex **1** was also treated with benzene at 70°C to give the diphenyltripalladium(II) complex. When the diisopropyl sulfide complex **1** was used in place of

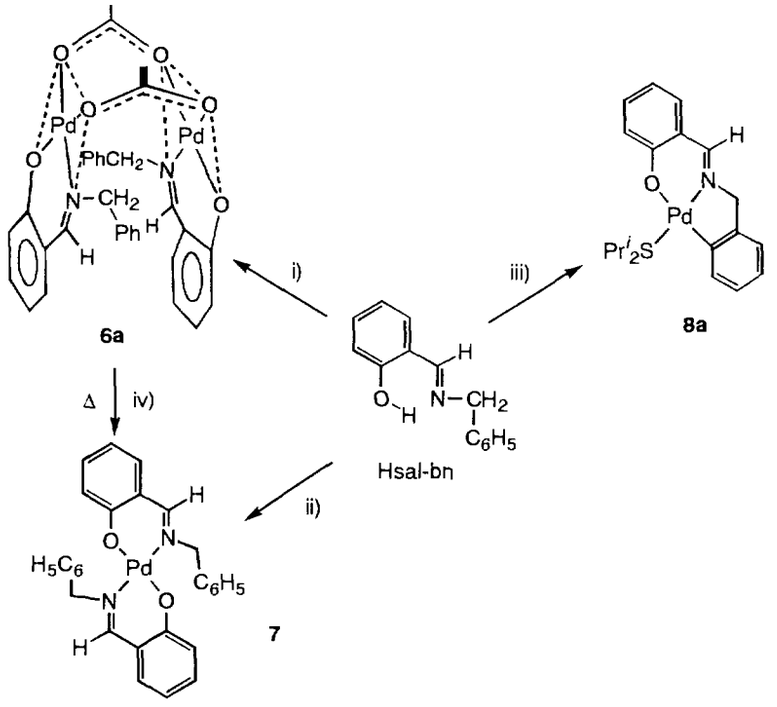
Table 3
^{1}H NMR data[a] of *N*-(salicylidene)benzylamines and their palladium complexes

Compound	Salicylidene moiety		Benzyl moiety		Others[b]
	ortho-Phenylene	N=CH	CH_2	Phenyl or *ortho*-phenylene	
Hsal-bn	6.86 (t, 7) 6.96 (d, 7) 7.24 (d, 7)	8.39	4.77 (2H)	7.27–7.36 (5H)[c]	13.39 (br) [OH]
6a	6.49 (t, 7.8, 2H) 6.65 (dd, 8.3, 1.5, 2H) 6.98 (d, 8.3, 2H) 7.24 (td, 8.3, 1.5, 2H)	6.36 (2H)	3.86 (d, 14.4, 2H) 4.72 (d, 14.4, 2H)	7.30–7.41 (10H)[c]	2.01 (6H) [CH_3CO_2]
7	6.54 (td, 7.8, 1, 2H) 6.82 (d, 7.8, 2H) 7.15 (dd, 7.8, 1.5, 2H) 7.21 (td, 7.8, 1.5, 2H)	7.71 (2H)	5.00 (4H)	7.25 (t, 8, 2H) 7.33 (t, 8, 4H) 7.44 (d, 8, 4H)	–
8a	6.52 (t, 8) 6.81 (d, 8) 7.00 (t, 7.3)[d] 7.10 (d, 7.3)[d]	8.11	5.12 (2H)	7.06 (t, 7.3)[d] 7.24 (d, 6.1)[d] 7.28 (t, 7.3)[d] 7.52 (d, 7.9)	1.50 (d, 6.7, 12H) [CH_3] 3.66 (sep, 6.7, 2H) [CH]
Hdcsal-bn	7.17 (d, 2.6) 7.41 (d, 2.6)	8.33	4.84 (2H)	7.31 (t, 7) 7.34–7.40 (4H)[c]	14.5 (br) [OH]
6b	6.60 (d, 2.7, 2H) 7.39 (d, 2.7, 2H)	6.63 (2H)	3.97 (d, 14.2, 2H) 4.83 (d, 14.2, 2H)	7.34–7.46 (10H)[c]	2.05 (6H) [CH_3CO_2]
8b	7.14 (d, 2.9) 7.44 (d, 2.9)	8.08	5.13 (2H)	7.00 (t, 7) 7.07 (t, 7) 7.09 (d, 7) 7.51 (d, 7)	1.50 (d, 6.6, 12H) [CH_3] 3.76 (sep, 6.6, 2H) [CH]
9	7.14 (d, 2.9) 7.46 (d, 2.9)	8.15 (dt, 19.8, 1.6)5.12 (br,2H)		6.96 (td, 7, 1.0) 7.09 (td, 7, 1.0) 7.13 (dd, 8, 2.2) 7.49 (dd, 8, 5.3)	3.93 (d, 12.5, 9H) [CH_3O]
10	7.06 (d, 3) 7.38 (d, 3)	7.61 (br)	5.17 (2H)	7.35 (td, 7, 1.5) 7.65 (dd, 7, 1.5) 7.70 (td, 7, 1.5) 7.74 (dd, 7, 1.5)	3.77 (d, 11, 3H) [CH_3O] 7.46(tdd, 7, 3.5, 1.4, 4H)[*meta*-H] 7.53 (tq, 7, 1.4, 2H) [*para*-H] 7.82 (ddt, 12, 7, 1.4, 4H) [*ortho*-H]
11	7.04 (d, 2.3) 7.40 (d, 2.3)	8.50	4.75 (2H)	7.35–7.45 (5H)[c]	1.93 (3H) [CH_3CO_2] 2.32 (6H) [CH_3] 8.35 (2H) [2, 6-H of dmpy]
12[e]	7.13 (d, 2.5, 2H) 7.40 (d, 2.5, 2H)	7.65 (2H)	5.17 (4H)	7.31 (t, 7, 2H) 7.35 (t, 7, 4H) 7.44 (d, 7, 4H)	–
13	6.98 (d, 2.9) 7.36 (d, 2.9)	7.40	4.76 (2H)	7.35–7.46 (m, 5H)[c]	1.26 (d, 6.5, 12H) [CH_3] 1.94 (3H) [CH_3CO_2] 3.38 (sep, 6.5, 2H) [CH]

[a]δ value from TMS at 30°C. Singlet and/or single proton in $CDCl_3$ unless noted in the parentheses. Multiplicity, coupling constant (Hz) and proton number of the other signal are given in the parentheses.
[b]Assignment of signal is presented in the brackets.
[c]Complicated signals due to phenyl group.
[d]Assignment of the signal is tentative.
[e]In CD_2Cl_2.

$Pd(MeCO_2)_2$, the resulting products changed dramatically. Complex **1** reacted with Hacac-bn in benzene at 50°C to give the yellow–khaki complex, [Pd(acac-$NCH_2C_6H_4$)(SPr^i_2)] (**4**) in a faily good yield. The ^{1}H NMR spectrum of **4** showed two triplets at δ 6.94 and 7.00 and two doublets at δ 7.07 and 7.50 with an equal intensity corresponding to 1H, which are characteristic of the cyclopalladated structure of the phenyl group. Furthermore, **4** exhibited a doublet at δ 1.46 (12H) and a septet at δ 3.54 (2H), assignable to isopropyl group, implying that one diisopropyl sulfide was coordinated with the palladium center. These data indicate that **4** is a mononuclear and bicyclic cyclopalladated complex, which has both an *O,N,C*-terdentate acac-$NCH_2C_6H_4$ moiety and one diisopropyl sulfide ligand. It is noteworthy that diisopropyl sulfide is coordinated as a neutral and unidentate ligand to the palladium(II) and assists the cyclopalladatoin of the benzyl group in the *N*-benzylated Schiff's base, which has a protic hydrogen.

Complex **4** was treated with PPh_3 in benzene at 50°C



Scheme 2. (i) $Pd(MeCO_2)_2$ at room temperature. (ii) $Pd(MeCO_2)_2$ at 50°C. (iii) $[Pd(MeCO_2)_2(SPr^i_2)_2]$ **1** at 50°C. (iv) Hsal-bn at 50°C.

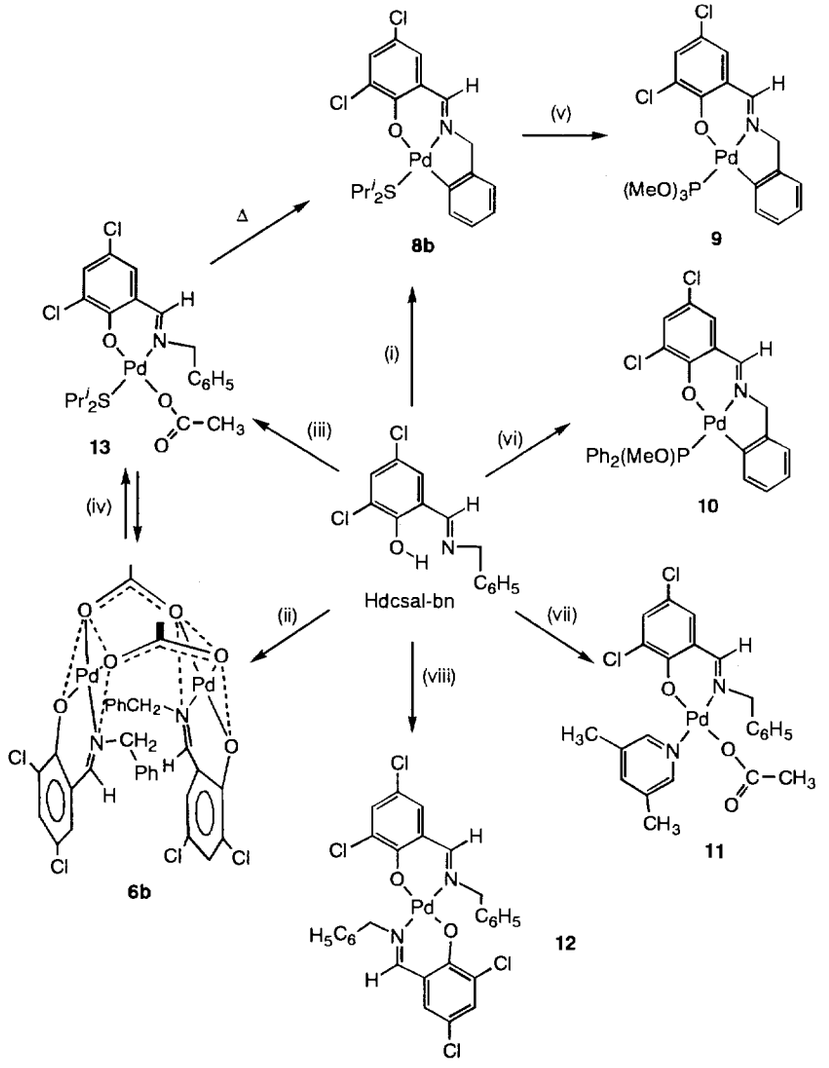
to give the pale yellow complex, [Pd(acac-$NCH_2C_6H_4$)(PPh_3)] (**5**). The ^1H NMR spectrum of **5** exhibited four signals corresponding to four *ortho*-phenylene protons in the range of δ 6.4–7.2. The $^{13}C\{^1H\}$ NMR spectrum showed two doublets at δ 146.2 and 140.0, in addition to three doublets due to *meta*-, *ortho*-, and *ipso*-carbons of the PPh_3 ligand. The first doublet at δ 146.2 was ascribed to a quaternary palladium-bonded carbon. The coupling constant 7.8 Hz was reasonable for *cis*-coupling to the coordinated PPh_3 ligand. These data confirm that the benzyl group of the acac-bn moiety was palladated at the *ortho*-position.

Complex **1** reacted with Hsal-bn in benzene at 50°C to afford the khaki–brown complex [Pd(sal-$NCH_2C_6H_4$)(SPr^i_2)] (**8a**) in 63% yield. The ^1H NMR spectrum of **8a** showed two doublets and two triplets, characteristic of the cyclopalladated structure of the phenyl group, in addition to the phenylene protons of the salicylidene moiety. These data and elemental analysis of **8a** indicate that **8a** has an *O,N,C*-terdentate sal-$NCH_2C_6H_4$ structure and one diisopropyl sulfide ligand. Similarly, when **1** was treated with Hdcsal-bn at 50°C, the *O,N,C*-terdentate complex **8b** was isolated in a fairly good yield (Scheme 3). The cyclopalladated complexes **4**, **5**, **8a**, and **8b** are fairly stable even in air owing to the bicyclic structure which consists of the five- and six-membered chelate rings Scheme 4).

The diisopropyl sulfide ligand in **8b** was easily substituted by trimethyl phosphite to afford **9** in a high yield. Its IR spectrum showed a very strong band at 1010 cm^{-1}, due to P–O–C bonds. The ^1H NMR spectrum showed a double doublet at δ 7.49 (1H) with a coupling to phosphorus atom with $J(HP) = 5.3$ Hz, supporting unambiguously the cyclometallated structure of the *ortho*-phenylene group. $Pd(MeCO_2)_2$ reacted with Hdcsal-bn in the presence of methyl diphenylphosphinite at 50°C to give the cyclometallated complex [Pd(dcsal-$NCH_2C_6H_4$){$PPh_2(OMe)$}] (**10**). The isolated yield was rather low because of its fairly good solubility towards the organic solvents. Methyl diphenylphosphinite was coordinated to the palladium center as a neutral, soft, and unidentate ligand and assisted the cyclopalladation of the benzyl group, like the case of diisopropyl sulfide (see below).

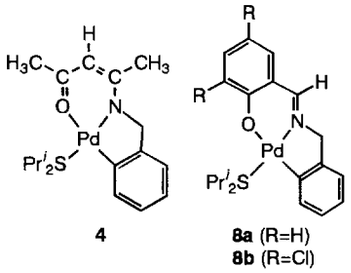
3.2.1. Reactions of 1 with Hdcsal-bn at 10°C

In order to confirm an intermediate in the reaction course from **1** and Hdcsal-bn to **8b**, reactions at 10°C were examined under several conditions. A benzene solution (20 cm^3) containing **1** (0.22 mmol), Hdcsal-bn (0.22 mmol), and diisopropyl sulfide (0.34 mmol) was kept at 10°C for 2 h. After concentration at reduced pressure, the resulting solution was diluted with hexane to give yellow solids (91 mg). The ^1H NMR spectrum of the solids revealed that they involved one main component and two minor ones. As for the main component, an AB-type quartet at δ 3.97 (2H) and 4.83 (2H) were ascribable to *N*-methylene protons, whereas a singlet at δ 2.05 (6H) was assignable to acetato methyl protons. The methine proton appeared also as a



Scheme 3. (i) $[Pd(MeCO_2)_2(SPr^i_2)_2]$ **1** at 50°C. (ii) $[Pd(MeCO_2)_3(SPr^i_2)]$ **1** at 10°C. (iii) $[Pd(MeCO_2)_2(SPr^i_2)_2]$ **1** in the presence of SPr^i_2 at 10°C. (iv) SPr^i_2. (v) $P(OMe)_3$. (vi) $Pd(MeCO_2)_2$ and $PPh_2(OMe)$ **1** at 50°C. (vii) $[Pd(MeCO_2)_2(dmpy)_2]$ **2** at 50°C. (viii) $[Pd(MeCO_2)_2(dmpy)_2]$ **2** in a half molar amount of Hdcsal-bn.

singlet (2H) at a considerably high field (δ 6.63). These data imply that the main component is an acetato-bridged dinuclear complex, $[Pd_2(dcsal\text{-}bn)_2(\mu\text{-}MeCO_2)_2]$ (**6b**),



Scheme 4. 2-Benzylamino-2-penten-4-one and *N*-(salicylidene)benzylamines reacted with $[Pd(MeCO_2)_2(SPr^i_2)_2]$ at 50°C to give *O,N,C*-bonded bicyclic cyclopalladated complexes, **4** and **8**, respectively.

which has a similar structure to **6a**. Moreover, the ^1H NMR spectrum involved two singlets at δ 1.94 (3H, CH_3CO_2) and 4.76 (2H, NCH_2) and a doublet at δ 1.26 (12H) and a septet at δ 3.38 (2H) due to two isopropyl groups. These signals were assigned to a mononuclear complex, $[Pd(dcsal\text{-}bn)(MeCO_2)(SPr^i_2)]$ (**13**), which had an analogous structure to $[Pd(dcsal\text{-}bn)(MeCO_2)(dmpy)]$ (**12**) (see below). The third component was **8b**. The molar ratio of **6b**:**13**:**8b** was about 82:9:9. It is noted that the cyclopalladation of Hdcsal-bn took place slowly even at 10°C.

Furthermore, when **1** (0.22 mmol) was treated with Hdcsal-bn (0.22 mmol) in the presence of 50 times molar amount of diisopropyl sulfide at 10°C for 0.5 h, the resulting solids (104 mg) consisted of **13** and **6b** in a molar ratio of about 82:18. The more the total amount of diisopropyl sulfide was present in the reaction mix-

ture, the more the diisopropyl sulfide complex **13** was formed, and vice versa. It seems that there is equilibrium among **6b**, **13**, and diisopropyl sulfide in solution. Several experiments to isolate **6b** and **13** in pure states resulted in failure.

A benzene solution (10 cm^3) containing both the mixture of **6b**, **13** and **8b** (45 mg, molar ratio of 82:9:9) and diisopropyl sulfide (0.17 mmol) was stirred at 50°C for 1 h. After analogous work-up, 38 mg of the orange solid, **8b** was obtained in 75% yield based on **6b** and **13**. Similarly, when a benzene solution of the mixture of **13** an **6b** (in the molar ratio of 82:18) was heated at 50°C for 1 h, **8b** was obtained in 85% yield based on **13**.

On the basis of these results, [Pd(dcsal-bn)($MeCO_2$)(SPr^i_2)] **13** is ascribed to the intermediate in the reaction from **1** and Hdcsal-bn to **8b**. The central palladium(II) in the intermediate attacks the benzyl group and metallated the *ortho*-carbon of the benzyl group to give **8b**, leaving acetic acid. Since diisopropyl sulfide is a soft ligand and prefers a soft metal such as palladium(II) [44], at least one sulfide ligand is ligated to the palladium as a neutral and unidentate ligand during the reaction course.

3.3. Reactions of [Pd($MeCO_2$)$_2$(dmpy)$_2$] 2 with the N-benzyl-substituted Schiff's bases

In order to compare the effects of dialkyl sulfide and a pyridine derivative on reaction pattern, reactions of **2** with the *N*-benzyl-substituted Schiff's bases were examined.

Equimolar amounts of **2** and Hacac-bn reacted at 50°C to give **3** (74% based on Hacac-bn), whereas **2** reacted with 2 times molar amount of Hsal-bn to afford **7** (87% based on Hsal-bn). In both the cases, the bis(*N,O*-chelate) complexes **3** and **7** were isolated as main products. When equimolar amounts of Hdcsal-bn and **2** were heated at 50°C in benzene, a yellow complex was formed. Its ^{1}H NMR spectrum showed two singlets at δ 1.93 (3H) and 2.32 (6H), which were ascribable to methyl protons of acetato ligand and those of 3,5-dimethylpyridine, respectively. Resonances characteristic of the dcsal-bn moiety were also observed. The IR spectrum showed two very strong bands near 1630 cm^{-1} and at 1310 cm^{-1}, assignable to asymmetric and symmetric stretching frequencies of the carboxylato ligand, respectively [45]. On the basis of these facts and the elemental analysis, the yellow complex was assigned to [Pd(dcsal-bn) ($MeCO_2$) (dmpy)] (**11**).

When the 3,5-dimethylpyridine-adduct **2** was used in place of **1**, no cyclopalladated complex was obtained at all. Although 3,5-dimethylpyridine is a neutral and unidentate ligand like diisopropyl sulfide, the basicity of the former is stronger than that of the latter. Therefore, dissociated 3,5-dimethylpyridine traps proton from Hacac-bn and Hsal-bn. The anions acac-bn and sal-bn formed by the proton trap promote the formation of the bis-*N,O*-chelate complexes **3** and **7**, respectively. On the other hands, the reaction between equimolar quantities of **2** and Hdcsal-bn formed the 3,5-dimethylpyridine adduct, **11**. The basicity of the dcsal-bn moiety is reduced in comparison with that of the sal-bn one owing to the two electron-withdrawing chloro substituents, and this corresponds well to the fact that the OH resonance of Hdcsal-bn showed a down-field shift compared with that of Hsal-bn in the ^{1}H NMR spectra (Table 3). This depresses the formation of the bis-*N,O*-chelate complex, [Pd(dcsal-bn)$_2$] (**12**). However, **2** reacted with 2 times molar amount of Hdcsal-bn at 50°C to give **12** in a moderate yield. These facts indicate that the molar ratio of the palladium(II) complex to the Schiff's base is an important factor to affect the product pattern.

Acknowledgements

Authors thank Shoei Chemical Industry for its financial support to the present study.

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