Pergamon

PII: S0277-5387(96)00564-5

Polyhedron Vol. 16, No. 14, pp. 2405–2411, 1997

0277-5387/97 $17.00+0.00

Synthesis and characterization of cyclopalladated complexes of secondary benzylamines

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(Received 22 August 1996; accepted 18 November 1996)

Abstract—Treating palladium acetate with secondary benzylamines $C_6H_5CH_2NHMe$ (**1**), $C_6H_5CH_2NHBu^n$ (**2**), $4\text{-}OCH_3C_6H_4CH_2NHBu^n$ (**3**), $3,4\text{-}(OMe)_2C_6H_3CH_2NHBu^n$ (**4**) and $2,4\text{-}(OMe)_2C_6H_3CH_2NHBu^n$ (**5**) in benzene gave acetato-bridged cyclopalladated complexes **1a–5a**. Metathesis reaction of these acetato-bridged cyclopalladated complexes (**1a–5a**) with LiCl in methanol gave chloro-bridged cyclopalladated complexes (**1a–5b**). The reactions of these chloro-bridged complexes were investigated with various ligands such as triphenylphosphine, acetylacetone, 1,1,2,2-tetraacetylethane, 1-phenylazo-2-naphthol and 2-hydroxy-3-*t*-butyl-5-methylbenzylidene-*p*-chloroaniline. The resulting complexes were analyzed by means of IR, ^1H NMR, ^{13}C NMR and ^1H-^1H COSY NMR spectroscopic techniques. © 1997 Elsevier Science Ltd

Keywords: cyclopalladation; secondary benzylamines; palladium acetate; triphenylphosphine; acetylacetone; tetraacetylethane; salen and azo ligands; COSY NMR.

Cyclopalladation is an important class of organometallic reaction and has been reviewed well [1]. Cyclopalladated complexes play a vital role in organic synthesis [2], photochemistry [3], homogeneous catalysis [4], optical resolution [5], liquid crystals [6] and antitumour agents [7]. Different types of nitrogen-containing ligands such as tertiary benzylamines, azines, oximes, heterocycles and Schiff bases have been used to synthesize cyclopalladated complexes. Cope and Friedrich first reported the synthesis of cyclopalladated chloro-bridged dimer of tertiary benzylamines by treating tertiary benzylamines with lithium tetrachloropalladate in methanol, whereas under similar conditions the corresponding secondary benzylamines did not give the expected cyclopalladated complex; instead a simple coordination complex of the type $PdCl_2L_2$ was obtained [8]. The primary benzylamines were also reported as weak ligands for cyclopalladation reaction. Recently Ryabov explained that the low reactivity of secondary benzylamine for cyclopalladation is due to strong initial coordination of the nitrogen atom of the secondary benzylamine to palladium [1d].

It is a well known fact that the mechanism of cyclopalladation is the initial coordination of nitrogen to metal followed by electrophilic substitution at the *ortho*-carbon atom. During cyclopalladation using Li_2PdCl_4 as starting material, the secondary benzylamine strongly coordinates to the metal, thereby reducing the electrophilicity of the metal atom towards substitution. This low electrophilicity of the palladium atom after initial coordination with secondary benzylamines retards the second step, i.e. electrophilic substitution, which would lead to the formation of the cyclopalladated complex. Steric factors are also responsible for the differences in reactivity of secondary and tertiary benzylamines, because tertiary benzylamines are more bulky than secondary benzylamines.

Due to this low reactivity of primary and secondary benzylamines, the reports on cyclopalladation chemistry of these ligands are scanty. Baba and Kawaguchi first reported the preparation of the cyclopalladated complex of primary benzylamine using $Pd(acac)_2$ as starting material in refluxing benzene [9]. The secondary benzylamines gave simple coordination complexes of the type $PdCl_2L_2$ with lithium tetrachloropalladate, whereas it was recently reported that α-substituted secondary benzylamines gave

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cyclopalladated complexes with lithium tetrachloropalladate [5b]. No explanation was given for the reactivity of α-substituted secondary benzylamine towards cyclopalladation in contrast to its α-unsubstituted analog. Fuchita and Tsuchiya prepared the cyclopalladated acetato-bridged complex of N-methylbenzylamine, a secondary benzylamine, by reacting it with palladium acetate in benzene [10]. Vicente *et al.* recently synthesized cyclopalladated complexes of α-alkyl primary benzylamines from its simple coordination complexes, $PdCl_2L_2$, by treating with $AgClO_4$ followed by treatment with alkali metal halide [11]. As a continuation of our interest in cyclopalladation chemistry [12a–12c], we report here the systematic study of cyclopalladation of various secondary benzylamines with palladium acetate and the reactions of cyclopalladated complexes with various ligands such as phosphines, acetylacetone, 1,1,2,2-tetraacetylethane, 2-hydroxy-3-*t*-butyl-5-methylbenzylidine-*p*-chloroaniline and 1-phenylazo-2-naphthol.

EXPERIMENTAL

Solvents were purified by the standard method [13]. Palladium acetate was prepared from palladium sponge [14]. The secondary benzylamines (**1–5**) were prepared by reducing the corresponding Schiff bases by sodium borohydride in methanol. 1,1,2,2-Tetraacetylethane [15], 2-hydroxy-3-*t*-butyl-5-methylbenzaldehyde [16] and 1-phenylazo-2-naphthol [17] were prepared by a literature method. The ligand 2-hydroxy-3-*t*-butyl-5-methylbenzylidene-*p*-chloroaniline was prepared by refluxing an equimolar amount of *p*-chloroaniline and 2-hydroxy-3-*t*-butyl-5-methylbenzaldehyde in methanol for 1 h. Elemental analyses were carried out in a Heraeus CHN-O rapid elemental analyzer. IR spectra in the range 4000–400 cm^{-1} were recorded on a Shimadzu IR-470 spectrophotometer. IR spectra in the range 400–180 cm^{-1} were recorded as polyethylene discs using a Perkin–Elmer 983G spectrophotometer. ^1H, ^{13}C and ^1H-^1H COSY NMR spectra were taken in $CDCl_3$ solution with TMS as internal standard using a JEOL-JNM-GSX 400 spectrometer.

Synthesis of $[\{Pd(C_6H_4CH_2N(H)Me(OAc)\}_2]$ (**1a**)

N-methylbenzylamine (133 mg, 1.1 mmol) was stirred with palladium acetate (225 mg, 1 mmol) in benzene (20 cm^3) at 60°C for 24 h under N_2. The solvent was evaporated under reduced pressure and the residue was extracted with CH_2Cl_2. The CH_2Cl_2 was distilled out and the product (**1a**) was recrystallized from dichloromethane/hexane (225 mg, 79%). Similarly, other acetato-bridged complexes **2a–5a** were prepared.

Synthesis of $[\{Pd(C_6H_4CH_2N(H)Me(Cl)\}_2]$ (**1b**)

The acetato-bridged complex **1a** (571 mg, 1.0 mmol) was stirred with lithium chloride (100 mg, 2.4 mmol) in methanol (25 cm^3) for 24 h at room temperature. The product **1b** was filtered, washed with water, methanol and dried *in vacuo* (440 mg, 84%). Similarly, other complexes **2b–5b** were synthesized.

Synthesis of $[\{Pd(4\text{-}MeC_6H_3CH_2N(H)Bu^n)(PPh_3)Cl\}]$ (**2c**)

The chloro-bridged dimer **2b** (63.6 mg, 0.1 mmol) was stirred with triphenylphosphine (52.4 mg, 0.2 mmol) in dichloromethane (5 cm^3) for 2 h. The solution was filtered and the solvent was evaporated. The complex **2c** formed was recrystallized from dichloromethane/hexane (95 mg, 82%). Similarly, other complexes **3c–5c** were synthesized.

Synthesis of $[\{Pd(C_6H_4CH_2N(H)CH_3)(acac)\}]$ (**1d**)

The chloro-bridged complex **1b** (52.4 mg, 0.1 mmol) was added with stirring to a clear methanol (10 cm^3) solution of acetylacetone (200 mg, 0.2 mmol) and sodium hydroxide (8 mg, 0.2 mmol). Stirring was continued for 10 h at room temperature. The complex **1d** was filtered, dried and recrystallized from dichloromethane/methanol (50 mg, 77%). Similarly, other complexes **2d–5d** were prepared.

Synthesis of $[\{Pd(4\text{-}OMeC_6H_3CH_2N(H)Bu^n)((CO CH_3)_2C)\}_2]$ (**3e**)

The chloro-bridged dimer **3b** (66.8 mg, 0.1 mmol) was added to the clear solution of 1,1,2,2-tetraacetylethane (19.8 mg, 0.1 mmol) and sodium hydroxide (8 mg, 0.2 mmol) in methanol (10 cm^3) and stirred for 10 h at room temperature. The product **3e** was filtered, washed with methanol (2 cm^3) and recrystallized from dichloromethane/methanol (65 mg, 82%).

Synthesis of $[\{Pd(C_6H_4CH_2N(H)Me)(2\text{-}O\text{-}3\text{-}C(CH_3)_3\text{-}5\text{-}MeC_6H_2CH{=}N{-}C_6H_4{-}p{-}Cl)\}]$ (**1f**)

The chloro-bridged dimer **1b** (52.4 mg, 0.1 mmol) was added to a well stirred clear solution of 2-hydroxy-3-*t*-butyl-5-methylbenzylidene-*p*-chloroaniline (60.4 mg, 0.2 mmol) and sodium hydroxide (8 mg, 0.2 mmol) in methanol (10 cm^3). Stirring was continued for 10 h at room temperature. The yellow product **1f** formed was filtered, dried and recrystallized from dichloromethane/methanol (85 mg, 80%).

Table 1. Elemental and IR spectral data of complexes[a]

Complexes	Colour	C	H	N	IR data (cm^{-1})
1a	Yellow	41.8(42.0)	4.5(4.6)	4.1(4.9)	1575, 1421
2a	Yellow	49.3(49.2)	6.3(6.2)	4.2(4.1)	1573, 1411
3a	Yellow	47.1(47.0)	6.0(5.9)	4.1(3.9)	1563, 1435
4a	Yellow	46.5(46.5)	5.9(6.0)	3.6(3.6)	1582, 1417
5a	Yellow	46.4(46.5)	6.1(6.0)	3.7(3.6)	1587, 1428
1b	Pale yellow	36.5(36.7)	3.9(3.9)	5.4(5.4)	330, 264
2b	Pale yellow	45.2(45.3)	5.9(5.7)	4.5(4.4)	314, 278, 240
3b	Pale yellow	43.3(43.1)	5.4(5.4)	4.3(4.2)	315, 270
4b	Pale yellow	42.9(42.9)	5.5(5.5)	4.0(3.9)	300, 279
5b	Pale yellow	42.8(42.9)	5.7(5.5)	3.9(3.9)	330, 294
2c	White	62.2(62.1)	5.8(5.7)	2.5(2.4)	305
3c	White	60.4(60.4)	5.7(5.6)	2.4(2.4)	310
4c	White	59.6(59.4)	5.7(5.6)	2.3(2.4)	310
5c	White	59.6(59.4)	4.7(5.6)	2.3(2.2)	301
1d	White	47.9(47.9)	5.4(5.3)	4.4(4.3)	1596, 1510
2d	White	53.4(53.5)	6.5(6.6)	3.7(3.7)	1588, 1514
3d	White	51.3(51.3)	6.4(6.3)	3.6(3.5)	1575, 1513
4d	White	50.8(50.5)	6.4(6.4)	3.2(3.3)	1585, 1510
5d	White	50.1(50.5)	6.3(6.4)	3.4(3.3)	1588, 1509
3e	White	51.3(51.5)	6.2(6.1)	3.6(3.5)	1565[b], 1411[b], 1365[b]
1f	Yellow	59.2(59.2)	5.6(5.5)	5.4(5.3)	1613
1g	Dark pink	60.9(60.8)	4.5(4.5)	8.9(8.9)	
2g	Dark pink	63.6(63.5)	5.6(5.5)	8.0(7.9)	
3g	Dark pink	61.7(61.6)	5.4(5.4)	7.8(7.7)	
4g	Dark pink	60.5(60.5)	5.5(5.4)	7.4(7.3)	
5g	Dark pink	60.5(60.5)	5.5(5.4)	7.4(7.3)	

[a] The calculated values are given in parentheses.
[b] Corresponds to the bridging 1,1,2,2-tetraacetylethane group [12b].

Synthesis of [{Pd($C_6H_4CH_2N(H)Me$)(2-O-$C_{10}H_6$—N=N—C_6H_5)}] (**1g**)

The chloro-bridged dimeric complex **1b** (52.4 mg, 0.1 mmol) was added to a well stirred clear solution of 1-phenylazo-2-naphthol (49.6 mg, 0.2 mmol) and sodium hydroxide (8 mg, 0.2 mmol) in methanol (20 cm^3) and stirred for 10 h. The bright-red product **1g** was filtered, washed with methanol and recrystallized from dichloromethane/methanol (85 mg, 90%). Similarly, the other complexes **2g–5g** were synthesized.

RESULTS AND DISCUSSION

The secondary benzylamines $C_6H_5CH_2N(H)CH_3$ (**1**), 4-$CH_3C_6H_4CH_2N(H)Bu^n$ (**2**), 4-$OCH_3C_6H_4CH_2N(H)Bu^n$ (**3**), 3,4-$(OCH_3)_2C_6H_3CH_2N(H)Bu^n$ (**4**), 2,4-$(OCH_3)_2C_6H_3CH_2N(H)Bu^n$ (**5**) upon treatment with palladium acetate in benzene gave aceto-bridged cyclopalladated complexes (**1a–5a**). The solubility of these complexes is not enough to carry out NMR spectral analysis. The IR spectra of these complexes exhibit two bands at *ca* 1570 and 1420 cm^{-1}, which are characteristic of the bridged acetato group [18] (Table 1). The metathesis reaction of these complexes with lithium chloride in methanol gave the corresponding chloro-bridged complexes **1b–5b**. The chloro-bridged complexes are less soluble in common organic solvents. The far-IR spectra of the chloro-bridged complexes **1b–5b** exhibit two bands at *ca* 310 and 275 cm^{-1} and are in accordance with the proposed dimeric formula of these complexes [19] (Fig. 1). In order to characterize the insoluble complexes **1b–5b** and also to find out the reactivity, the reactions of these complexes with various ligands such as tri-

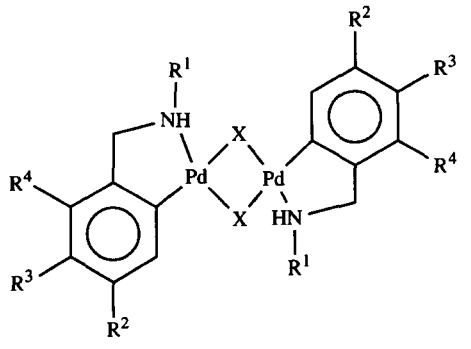

Fig. 1. **1**: R^1 = Me, $R^2 = R^3 = R^4$ = H; **2**: $R^1 = Bu^n$, R^2 = Me, $R^3 = R^4$ = H; **3**: $R^1 = Bu^n$, $R^2 = OCH_3$, $R^3 = R^4$ = H; **4**: $R^1 = Bu^n$, $R^2 = R^3 = OCH_3$, R^4 = H; **5**: $R^1 = Bu^n$, $R^2 = R^4 = OCH_3$, R^3 = H. **a**: X = OAc; **b**: X = Cl.

phenylphosphine, acetylacetone, 1,1,2,2-tetraacetylethane, 2-hydroxy-3-*t*-butyl-5-methylbenzylidene-*p*-chloroaniline and 1-phenylazo-2-naphthol were carried out.

The reaction of triphenylphosphine was carried out with the chloro-bridged complexes **2b–5b**. The resulting complexes are **2c–5c** (Fig. 2). The far-IR spectra of these complexes exhibit a strong band at *ca* 305 cm^{-1} corresponding to the Pd—Cl stretching frequency, suggesting that chlorine is *trans* to the palladated carbon atom [19]. The ^1H NMR spectra of complex **5c** suggest that the proton adjacent to the metallated carbon atom is shifted to high field (Table 2). A similar type of high-field shift was noticed in different cyclopalladated complexes earlier [12]. This high-field shift is due to diamagnetic shielding of triphenylphosphine. This also suggests that the triphenylphosphine is *trans* to the nitrogen atom. The ^{31}P NMR spectrum of this complex exhibits a peak at 40.65 ppm, suggesting that only one isomer was the product after the bridge-splitting reaction with triphenylphosphine.

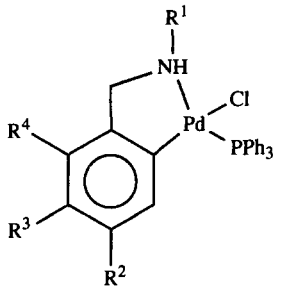

Fig. 2. **2c**: $R^1 = Bu^n$, $R^2 = Me$, $R^3 = R^4 = H$; **3c**: $R^1 = Bu^n$, $R^2 = OCH_3$, $R^3 = R^4 = H$; **4c**: $R^1 = Bu^n$, $R^2 = R^3 = OCH_3$, $R^4 = H$; **5c**: $R^1 = Bu^n$, $R^4 = OCH_3$, $R^3 = H$.

The bridge-splitting reaction of the chloro-bridged complexes **1a–5b** was also carried out with acetylacetone. The chloro-bridged complex **1b** gave **1d** with

Table 2. ^1H and ^{13}C NMR spectral data of complexes

5c ^1H NMR: δ 0.97 (t, 3H, Ch_3), 1.38 (m, 2H, CH_2), 1.75 (m, 2H, CH_2), 2.85 (s, 3H, OCH_3), 3.10 (m, 2H, CH_2), 3.70 (s, 3H, OCH_3), 4.15 (s, 1H, NH), 4.30 (m, 2H, H^7), 5.52 (dd, 1H, H^3), 6.00 (d, 1H, H^5), 7.35 (m, 6H), 7.41 (m, 3H), 7.70 (m, 6H). ^{13}C NMR: δ 13.86 (q, CH_3), 20.11 (t, CH_2), 52.28 (t, CH_2), 54.50 (q, OCH_3), 54.63 (q, OCH_3), 55.01 (t, C^7), 95.26 (d, C^5), 113.62 (d, C^3), 128.04 (d), 130.59 (d), 130.83 (s, C^1), 131.31 (s), 135.23 (d), 151.91 (s, C^2), 154.58 (s, C^4), 156.68 (s, C^6). ^{31}P NMR (CH_2Cl_2): δ 40.65.

1d ^1H NMR: δ 1.91 (s, 3H, H^8), 2.0 (s, 3H, H^2), 2.65 (d, 3H, NCH_3), 3.81 (m, 2H, H^7), 4.00 (bs, 1H, NH), 5.30 (s, 1H, H^{10}), 6.80 (d, 1H, H^6), 6.95 (m, 2H, H^4+H^5), 7.28 (d, 1H, H^3).

2d ^1H NMR: δ 0.95 (t, 3H, CH_3), 1.35 (m, 2H, CH_2), 1.70 (m, 2H, CH_2), 1.90 (s, 3H, H^8), 2.00 (s, 3H, H^{12}), 2.30 (s, 3H, CH_3), 2.90 (m, 2H, CH_2), 3.85 (m, 2H, H^7), 4.05 (bs, 1H, NH), 5.27 (s, 1H, H^{10}), 6.75 (dd, 2H, H^5+H^6), 7.07 (s, H^3). ^{13}C NMR: δ 13.87 (q, CH_3), 20.19 (t, CH_2), 21.46 (q, CH_3), 27.70 (q, C^8), 27.98 (q, C^{12}), 30.07 (t, CH_2), 52.69 (t, CH_2), 60.58 (t, C^7), 99.91 (d, C^{10}), 120.19 (d, C^6), 124.94 (d, C^5), 131.10 (d, C^3), 133.93 (s, C^4), 145.31 (s, C^1), 145.52 (s, C^2), 186.26 (s, C^9), 187.63 (s, C^{11}).

3e ^1H NMR: δ 0.95 (t, 3H, CH_3), 1.38 (m, 2H, CH_2), 1.80 (m, 2H, CH_2), 1.90 (s, 3H, H^8), 2.00 (s, 3H, H^{12}), 3.00 (m, 2H, CH_2), 3.80 (s, 3H, OCH_3), 4.00 (m, 2H, H^7), 4.05 (bs, 1H, NH), 6.55 (dd, 1H, H^5), 6.80 (d, 1H, H^6), 6.90 (s, 1H, H^3). ^{13}C NMR: δ 13.89 (q, CH_3), 20.13 (t, CH_2), 28.31 (q, C^8+C^{12}), 30.16 (t, CH_2), 52.93 (t, CH_2), 55.16 (q, OCH_3), 60.61 (t, C^7), 110.66 (d, C^6), 112.87 (s, C^{10}), 114.91 (d, C^5), 121.07 (d, C^3), 140.42 (s, C^1), 147.43 (s, C^2), 156.13 (s, C^4), 187.05 (s, C^9), 189.12 (s, C^{11}).

1f ^1H NMR: δ 1.43 (s, 9H, H^{20}), 2.20 (s, 3H, H^{19}), 2.85 (d, 3H, NCH_3), 3.65 (bs, 1H, NH), 3.90 (dd, 1H, H^7), 4.40 (dd, 1H, H^7), 5.75 (d, 1H, H^3), 6.46 (t, 1H, H^4), 6.77 (t, 1H, H^5), 6.85 (s, 1H, H^{12}), 6.87 (d, 1H, H^6), 7.18 (d, 2H, H^{16}), 7.22 (s, 1H, H^{10}), 7.28 (d, 2H, H^{17}), 7.89 (s, 1H, H^{14}). ^{13}C NMR: δ 20.46 (q, C^{19}), 29.58 (q, C^{20}), 35.20 (s, C^{21}), 40.94 (q, NCH_3), 63.99 (t, H^7), 120.34 (s, C^{11}), 121.05 (d, C^6), 121.54 (s, C^{13}), 122.95 (d, C^5), 124.27 (d, C^4), 126.84 (d, C^{16}), 128.31 (d, C^{17}), 131.41 (s, C^{18}), 133.17 (d, C^3), 134.05 (d, C^{10}), 135.15 (d, C^{12}), 140.54 (s, C^9), 148.42 (s, C^1), 149.04 (s, C^8), 153.23 (s, C^{15}), 165.57 (s, C^2), 166.83 (d, C^{14}).

4g ^1H NMR: δ 0.92 (t, 3H, CH_3), 1.37 (m, 2H, CH_2), 1.75 (m, 2H, CH_2), 3.00 (m, 2H, CH_2), 3.20 (s, 3H, OCH_3), 3.65 (s, 3H, OCH_3), 3.92 (m, 2H, H^7), 4.15 (m, 1H, NH), 5.60 (s, 1H, H^3), 6.40 (s, 1H, H^6), 6.95 (d, 1H, H^9), 7.20 (t, 1H, H^{13}), 7.28 (m, 3H, $H^{20}+H^{21}$), 7.52 (t, 1H, H^{14}), 7.60 (d, 1H, H^{12}), 7.66 (d, 1H, H^{10}), 7.98 (d, 2H, H^{19}), 8.38 (d, 1H, H^{15}). ^{13}C NMR: δ 13.89 (q, CH_3), 20.16 (t, CH_2), 30.39 (t, Ch_2), 52.61 (t, CH_2), 55.09 (q, OCH_3), 55.65 (q, OCH_3), 60.63 (t, C^7), 104.84 (d, C^6), 118.32 (d, C^3), 122.04 (d, C^9), 123.45 (d), 125.21 (d), 125.27 (d), 125.93 (s, C^{17}), 127.12 (d), 127.53 (d), 127.87 (d), 128.07 (d), 133.97 (s, C^{11}), 134.82 (s, C^{16}), 136.99 (d), 138.37 (s, C^4), 139.88 (s, C^5), 144.76 (s, C^1), 145.55 (s, C^8), 156.13 (s, C^{18}), 157.12 (s, C^2).

^1H and ^{13}C spectra of all complexes are recorded in $CDCl_3$ solution with TMS as internal standard. The ^{13}P NMR is recorded in CH_2Cl_2 with 85% H_3PO_4 as external standard.

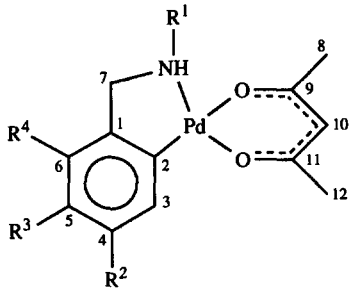

Fig. 3. **1d**: $R^1 = Me$, $R^2 = R^3 = R^4 = H$; **2d**: $R^1 = Bu^n$, $R^2 = Me$, $R^3 = R^4 = H$; **3d**: $R^1 = Bu^n$, $R^2 = OCH_3$, $R^3 = R^4 = H$; **4d**: $R^1 = Bu^n$, $R^2 = R^3 = OCH_3$, $R^4 = H$; **5d**: $R^1 = Bu^n$, $R^2 = R^4 = OCH_3$, $R^3 = H$.

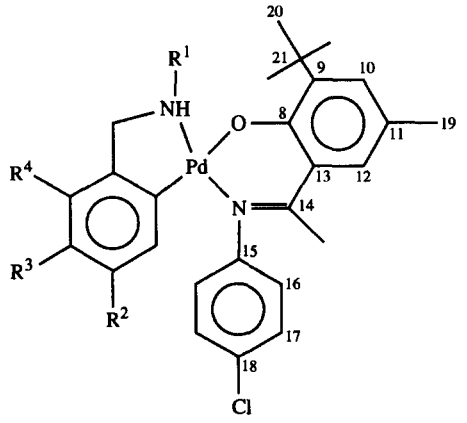

Fig. 5. **1f**: $R^1 = Me$, $R^2 = R^3 = R^4 = H$.

acetylacetone in the presence of a base in methanol. Similarly, other complexes **2d–5d** were synthesized from **2b–5b** (Fig. 3). These complexes exhibit two strong bands at *ca* 1590 and 1510 cm^{-1} in their IR spectra which are characteristic of acetylacetonato moiety coordinated with metal atom. The ^1H NMR spectra of complexes **1d** and **2d** suggest that both the methyl groups of acetylacetonate moiety are not magnetically equivalent (Table 2). Similar to acetylacetone, the ligand 1,1,2,2-tetraacetylethane gave complex **3e** with **3b** in the presence of a base in methanol (Fig. 4).

The bridge-splitting reaction of chloro-bridged complexes **1b-5b** was extended to the ligands, 2-hydroxy-3-*t*-butyl-5-methylbenzylidene-*p*-chloroaniline and 1-phenylazo-2-naphthol in methanol in the presence of a base. The complex **1b** gave **1f** with 2-hydroxy-3-*t*-butyl-5-methylbenzylidene-*p*-chloroaniline (Fig. 5). The IR spectrum of complex **1f** exhibits a strong band at 1613 cm^{-1} corresponding to the asymmetric stretching frequency of the C=N bond. The asymmetric stretching frequency of the C=N bond of the free ligand 2-hydroxy-3-*t*-butyl-5-methylbenzylidene-*p*-chloroaniline is 1627 cm^{-1}. This low shift in frequency suggests that the nitrogen atom is coordinated to the metal atom [18,20]. The ^1H NMR spectrum of complex **1f** suggests that the CH=N proton was shifted to high field after complexation also confirming the coordination of nitrogen to the metal, whilst the proton adjacent to the metallated carbon atom was shifted to high-field and appeared at 5.75 ppm. This high-field shift could be due to the diamagnetic shielding of the *p*-chlorophenyl ring of the complex [12]. This also suggests that both the nitrogen atoms are in a *trans* disposition. Recently Ghedini *et al.* carried out bridge-splitting reactions of cyclopalladated chloro-bridged dimers of azobenzenes with salen-based ligands and observed the formation of *cis* and *trans* isomers [21]. We noticed only one set of signals in the ^1H NMR and ^{13}C NMR spectra of complex **1f**, suggesting the exclusive formation of only one isomer (Table 2). The high-field shift of the proton adjacent to the metallated carbon atom suggests that the complex formed was a *trans* isomer.

Similarly to 2-hydroxy-3-*t*-butyl-5-methylbenzylidene-*p*-chloroaniline, the other ligand 1-phenylazo-2-naphthol reacted with the chloro-bridged dimer **1b–5b** in methanol in the presence of a base to give dark red complexes **1g–5g** (Fig. 6). The ^1H NMR spectra of complexes **1g** and **4g** suggest that the proton adjacent to the metallated carbon atom was shifted to high-field, similar to that noticed in complex **1f**. This shift is due to diamagnetic shielding of the phenyl group of 1-phenylazo-2-naphthol. This also suggests that both

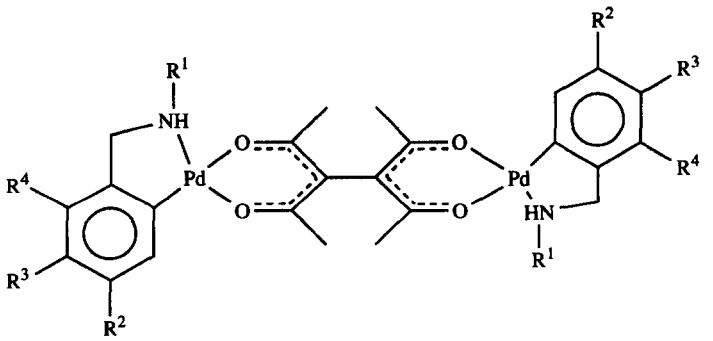

Fig. 4. **3e**: $R^1 = Bu^n$, $R^2 = OCH_3$, $R^3 = R^4 = H$.

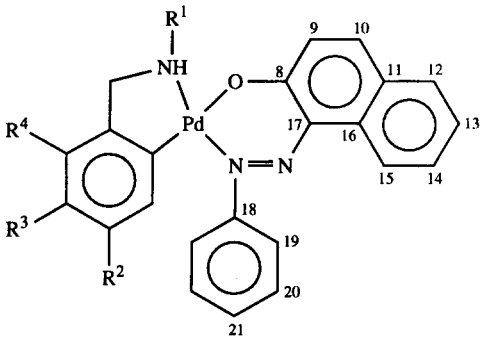

Fig. 6. **1g**: R^1 = Me, $R^2 = R^3 = R^4$ = H; **2g**: R^1 = Bu^n, R^2 = Me, $R^3 = R^4$ = H; **3g**: R^1 = Bu^n, R^2 = OCH_3, $R^3 = R^4$ = H; **4g**: R^1 = Bu^n, $R^2 = R^3$ = OCH_3, R^4 = H; **5g**: R^1 = Bu^n, = R^4 = OCH_3, R^3 = H.

the nitrogen atoms are in the *trans* disposition in the complex [12]. We have carried out homonuclear correlated two-dimensional NMR (COSY) spectroscopic investigation of complexes **1f** and **1g** in order to elucidate the structure of these complexes and also to confirm the *trans* disposition of both the nitrogen atoms. The two-dimensional ^1H-^1H chemical shift correlation spectrum of one of the complex **1g** is given (Fig. 7). The assignment of the peaks was made based on the literature [12b].

Acknowledgements—We thank the Catalysis Division, Department of Chemistry and Regional Sophisticated Instrumentation Centre I.I.T., Madras, for instrumental analysis. We also thank Mr M.S. Moni for recording the

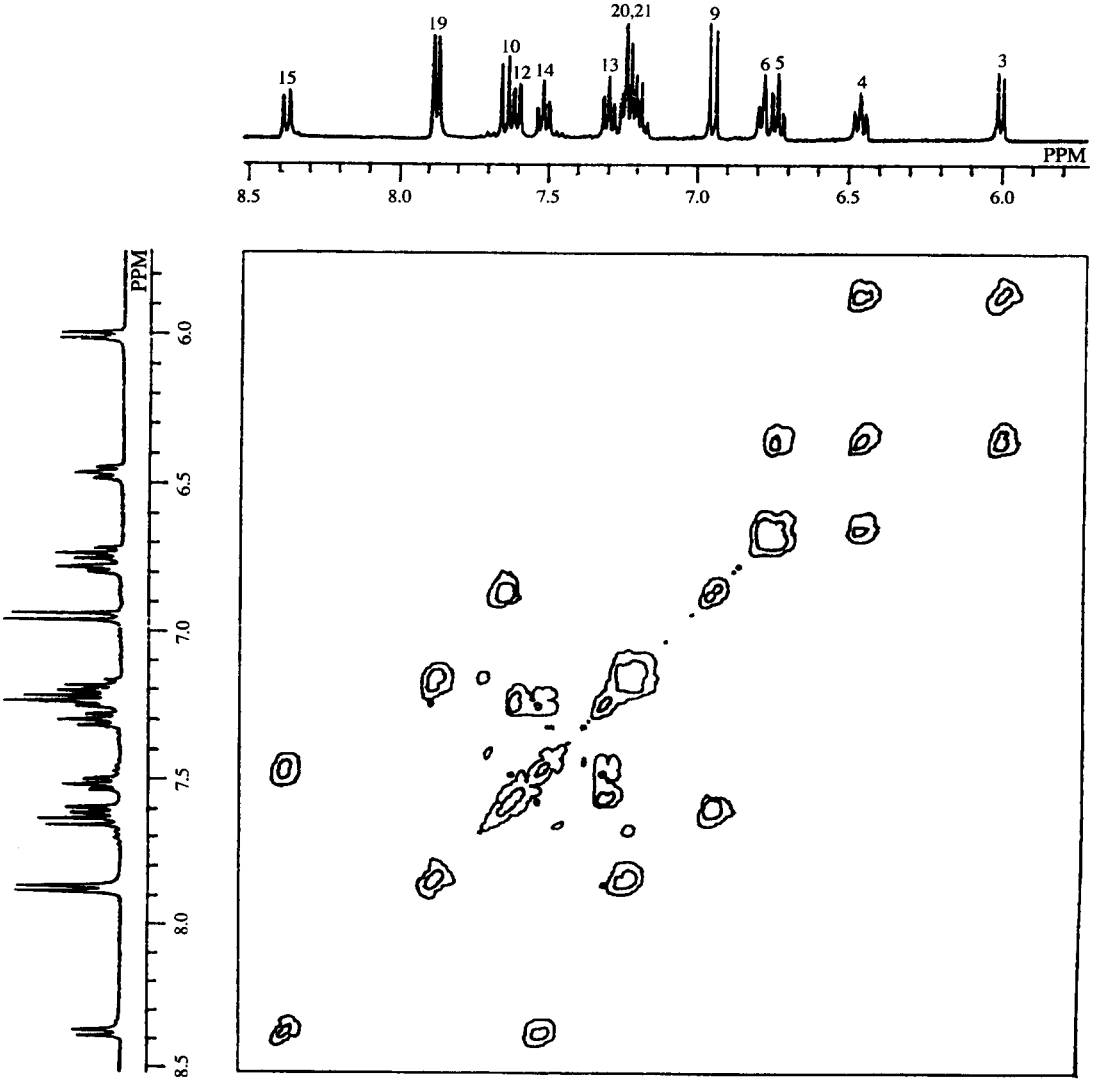

Fig. 7. ^1H-^1H COSY NMR spectrum of complex **1g**.

NMR spectra of complexes. One of the authors (K.S) thanks I.I.T., Madras, for financial assistance and a research fellowship.

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