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Synthesis and characterisation of cyclopalladated complexes of α-tetraloneketimine

K SELVAKUMAR and S VANCHEESAN*

Department of Chemistry, Indian Institute of Technology, Madras 600036, India

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Abstract. The reactions of various α-tetraloneketimines(L) with palladium acetate in $CHCl_3$ have been studied. In all cases acetato-bridged dimeric compound $[Pd_2L_2(OAc)_2]$ were obtained in which metallation had occurred at the *peri* position of the α-tetralone nucleus. The analogous chloro-bridged compounds $[Pd_2L_2Cl_2]$ were prepared from acetato-bridged dimer by metathesis reaction using LiCl. The bridge-splitting reaction of $[Pd_2L_2Cl_2]$ with triphenylphosphine, acetylacetone, methylacetoacetate, diethyldithiocarbamate, 2,2′-bipyridine, 1,10-phenanthroline, 4,4′-bipyridine and 2,2′-penta and hexamethylenebipyridine have been studied. The reactivity of 4,4′-bipyridine and 2,2′-penta and hexamethylene-bipyridines have also been studied with di-μ-chloro *bis*[N,N-dimethylbenzylamine C^2,N]dipalladium(II) and di-μ-chloro *bis*[N-benzylidenemethylamine C^2,N] dipalladium(II). All the complexes obtained were characterised by elemental analysis, IR, ^1H NMR and ^{13}C NMR spectroscopy.

Keywords. α-Tetraloneketimine; cyclopalladated complexes; monopalladated binuclear complexes.

1. Introduction

Cyclometallation is an important area of current interest in organometallic chemistry, in particular cyclopalladation of N-donor ligands like amines, amidines, azines, hydrazones, heterocycles, oximes and Schiff bases (Constable 1984; Newkome *et al* 1986; Ryabov 1990). Cyclopalladated complexes are used as valuable starting materials for regio and stereo selective organic synthesis (Ryabov 1985), asymmetric synthesis (Sokolov 1983), catalysis (Bose and Saha 1989), photochemistry (Wakatsuki *et al* 1985) and also used as an important constituent of ordered mesophases (Bruce 1993).

Schiff bases are suitable ligands for cyclometallation reactions. Pericyclometallation, found to be least favourable, were reported in the cases of amines (Phillips and Steel 1991), oximes (Nielson 1981) and azo compounds (Hugentobler *et al* 1982). To the best of our knowledge pericyclometallation of Schiff bases have not been reported. Moreover, bridge-splitting reactions of chloro-bridged dimer with *bis*(diphenylphosphino) alkanes and alkenes to prepare monometallated binuclear complexes had been extensively studied (Vila *et al* 1993), but only scanty reports are available in the literature about the bridge-splitting reaction using 4,4′-bipyridine (Newkome *et al* 1982) and 2,2′-polymethylenebipyridines. We report the synthesis and characterization of pericyclopalladated complexes of α-tetraloneketimine and novel monometallated

*For correspondence

binuclear complexes of N,N′-dimethylbenzylamine, N-benzylidenemethylamine and α-tetraloneketimine using 4,4′-bipyridine and 2,2′-polymethylenebipyridine.

2. Experimental

Solvents were purified by the standard method (Perrin and Armarego 1988). $Pd(OAc)_2$ was prepared from palladium sponge (Stephenson *et al* 1965). Elemental analysis was carried out in Heraeus CHN-O rapid elemental analyzer. Infrared spectra in the range of 4000–400 cm^{-1} were recorded using Shimadzu IR-470 spectrophotometer in KBr disc. IR spectra in the range of 400–200 cm^{-1} were recorded using Perkin Elmer 983G spectrophotometer in polyethylene disc. ^1H NMR and ^{13}C NMR were recorded using JEOL JNMGSX 400 spectrometer. All the ^1H NMR and ^{13}C NMR spectra were either taken in $CDCl_3$ or DMSO-d_6 solution with tetramethylsilane as the internal standard. 2,2′-Penta and hexamethylenebipyridine (Jampolsky 1952), di-μ-chloro-*bis*[N,N-dimethylbenzylamine C^2,N]dipalladium(II) (V) (Cope and Friedrich 1968) and di-μ-chloro*bis*[N-benzylidenemethylamine C^2,N] dipalladium(II) (VI) (Onoue and Moritini 1972) were prepared according to the literature method.

2.1 *Preparation of ligands*

All the ligands (I-IV) were prepared by refluxing α-tetralone with appropriate amine in benzene in the presence of *p*-toluenesulphonic acid for 48 h in a Dean–Stark apparatus.

^1H NMR(I, $CDCl_3$) 1·87(2H, *m*, C^6H), 2·46(2H, *t*, C^5H), 2·83(2H, *t*, C^7H), 6·7(2H, *d*, $C^{12}H$), 6·97(1H, *t*, $C^{14}H$), 7·1(1H, *d*, C^4H), 7·25(4H, *m*, $C^2H + C^3H + C^{13}H$), 8·28(1H, *d*, C^1H). ^{13}C NMR 22·85(C^6), 29·63(C^5), 29·83(C^7), 119·16(C^{12}), 122·65(C^{14}), 126·15, 126·5, 128·28(aromatic), 128·61(C^{13}), 130·24(C^1), 133·73(C^{10}), 140·66(C^9), 151·49(C^{11}) 164·43 (C^8).

2.2 *Preparation of complexes*

2.2a *Synthesis of acetato-bridged dimer*: Schiff base I (243 mg, 1·1 mmol) was stirred with palladium acetate (225 mg, 1 mmol) in 10 ml of chloroform for 5 h under nitrogen at room temperature. The dark greenish-yellow solution was filtered, concentrated and chromatographed on silica gel using dichloromethane–methanol (1%) as eluent. The yellow fraction is collected and evaporated. The complex Ia obtained is recrystallised from dichloromethane/hexane (290 mg, 75%).

^1H NMR($CDCl_3$) 1·40(3H, *s*, $COOCH_3$), 1·72(2H. *t*, C^5H), 2·25(2H, *m*, C^6H), 2·64 (2H, *t*, C^7H), 6·84(1H, *d*, C^2H), 7·0(3H, *m*, $C^4H + C^{12}H$), 7·1(1H, *t*, $C^{14}H$), 7·2(1H, *t*, C^3H), 7·3(2H, *t*, $C^{13}H$), ^{13}C NMR 23·18(CH_3), 23·71(C^6), 28·461(C^5), 29·948(C^7), 123·2(C^{12}), 124·4(C^{14}), 126·3(C^4), 128·1(C^{13}), 129·9(C^3), 131(C^2), 141·9(C^{10}), 144·4(C^9), 145·4(C^{11}), 156·4(C^1) 180·5(CO), 182·4(C^8). Similarly IIa, IIIa and IVa were prepared respectively from II, III and IV.

2.2b *Synthesis of chloro-bridged dimer*: The complex Ia (771 mg, 0·1 mmol) was refluxed with lithiumchloride (93·5 mg, 2·2 mmol) in 20 ml of methanol for 1 h with stirring. The pale yellow complex Ib obtained was filtered, washed with water, methanol, ether and then dried under vacuum (670 mg, 92·5%). Similarly IIb, IIIb and IVb were prepared from IIa, IIIa and IVa.

2.3 *Bridge-splitting reaction*

2.3a *Reaction with triphenylphosphine*: The chloro-bridged dimer Ib (72 mg, 0·1 mmol) was stirred with triphenylphosphine (52 mg, 0·2 mmol) in 5 ml of dichloromethane for 1 h. The resultant clear solution was filtered and concentrated. The complex Ic obtained was recrystallised from chloroform/hexane (110 mg, 88%).

2.3b *Reaction with acetylacetone:* To the stirred suspension of Ib (72 mg, 0·1 mmol) in 2 ml of methanol was added acetylacetone (20 mg, 0·2 mmol) and sodium (4·6 mg, 0·2 mmol) in 3 ml methanol. The pale yellow complex obtained after stirring for 10 h at room temperature was filtered and washed with 3 × 2 ml of methanol. The complex Id obtained is recrystallised from dichloromethane/ methanol (75 mg, 88%).

^{1}H NMR($CDCl_3$) 1·68(3H, *s*, $C^{15}H$), 1·87(2H, *m*, C^6H), 2·02(3H, *t*, $C^{19}H$), 2·55(2H, *t*, C^5H), 2·75(2H, *t*, C^7H), 5·2(1H, *s*, $C^{17}H$), 6·84(1H, *d*, C^2H), 7·15(3H, *m*, $C^{12}H$ + $C^{14}H$), 7·25(1H, *m*, C^6H), 7·4(3H, *m*, $C^{13}H$) + C^4H). ^{13}C NMR 24·4(C^6), 28·0(C^{15}), 28·3(C^{19}), 29·2(C^5), 31·0(C^7), 100·66(C^{17}), 124·3(C^{14}), 124·7(C^{12}), 127·0(C^4), 128·9(C^{13}), 129·4(C^3). 131·4(C^2), 142·8(C^{10}), 145(C^9), 145·6(C^{11}), 158·6(C^1), 184·4(C^8), 186·3(C^{16}), 188·8(C^{18}).

2.3c *Reaction with methylacetoacetate*: To the stirred suspension of Ib (72 mg, 0·1 mmol) in 2 ml of methanol was added methylacetoacetate (23 mg, 0·2 mmol) and KOH (11 mg, 0·2 mmol) in 3 ml of methanol. The stirring was continued for further 5 h at room temperature. The complex Ie was filtered, washed with (3 × 2) ml of methanol and recrystallised from dichloromethane/methanol (79 mg, 89%).

^{1}H NMR($CDCl_3$) 1·9(2H, *m*, C^6H), 2·0(3H, *s*, $C^{15}H$), 2·54(2H, *t*, C^5H), 2·74(2H, *t*, C^7H), 3·0(3H, *s*, $C^{19}H$), 4·7(1H, *s*, $C^{17}H$), 6·84(1H, *d*, C^2H), 7·15(3H, *m*, $C^{12}H$ + $C^{14}H$), 7·24(1H, *m* C^3H), 7·36(3H, *m*, $C^{13}H$ + C^4H). ^{13}C NMR 23·7(C^6), 27·2(C^{15}), 28·4(C^5), 30·1(C^7), 50·7(C^{19}), 84·5(C^{17}), 123·7(C^{14}), 123·8(C^{12}), 126·3(C^4), 128·6(C^{13}), 128·8(C^3), 130·9(C^2), 142·3(C^{10}), 144·2(C^9), 145·4(C^{11}), 156·3(C^1), 170·9(C^{16}), 183·4(C^8), 186·7(C^{18}).

2.3d *Reaction with diethyldithiocarbamate*: The chloro-bridged dimer Ib (72 mg, 0·1 mmol) was stirred with sodiumdiethyldithiocarbamate (45 mg, 0·2 mmol) in 5 ml methanol for 10 h at room temperature. The yellow complex If formed was filtered, washed with methanol and recrystallised from dichloromethane/methanol (87 mg, 92%).

^{1}H NMR($CDCl_3$) 1·15, 1·25(6H, 2*t*, $C^{17}H$ + $C^{19}H$), 1·9(2H, *m*, C^6H), 2·6(2H, *t*, C^5H), 2·75(2H, *t*, C^7H), 3·7, 3·75(4H, 2*q*, $C^{16}H$ + $C^{18}H$) 6·85(1H, *d*, C^2H), 6·98(1H, *d*, C^4H), 7·08 (1H, *t*, C^3H), 7·15(3H, *m*, $C^{12}H$ + $C^{14}H$), 7·37(2H, *t*, $C^{13}H$). ^{13}C NMR 12·4(C^{17}), 12·5 (C^{19}), 23·8(C^6), 28·89(C^5), 30·6(C^7), 44·2(C^{16}), 45·5(C^{18}), 122·9(C^{12}), 123·6(C^{14}), 126·0(C^4), 128·9(C^{13}), 131·4(C^3), 131·5(C^2), 142·9(C^9), 144·9(C^{10}), 147·9(C^{11}), 161·7(C^1), 182·8(C^8), 209·4(C^{15}).

2.3e *Reaction with 2,2′-bipyridine*: The chloro-bridged dimer Ib (72 mg, 0·1 mmol) was stirred with $AgClO_4$ (42 mg, 0·2 mmol) in 5 ml of acetonitrile for 1 h. The silver chloride formed was filtered out. The filtrate was concentrated by evaporating under vacuum. The residue was stirred with bipyridine (32 mg, 0·2 mmol) in 5 ml of methanol for 2 h. The pale yellow complex Ig was filtered, washed with methanol and dried under vacuum (105 mg, 90%).

^{1}H NMR(DMSO-d_6) 1·95(2H, *m*, C^6H), 2·65(2H, *t*, C^5H), 2·81(2H, *t*, C^7H), 7·1(2H, *d*, $C^{12}H$), 7·3(1H, *t*, $C^{14}H$), 7·6(9H, *m*, $C^{16}H$ + $C^{18}H$ + $C^{13}H$ + C^2H + C^3H + C^4H),

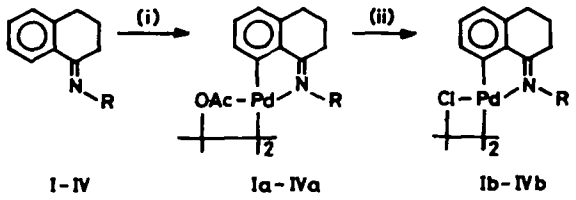
Table 1. Microanalytical data, colour and melting point.

Complex	Colour	Elements			m.p.# (°C)
		C	H	N	
Ia	Yellow	55·83 (56·04)	4·44 (4·44)	3·57 (3·63)	256
Ib	Pale yellow	52·86 (53·06)	3·92 (3·90)	3·76 (3·87)	210
Ic	White	65·01 (65·39)	4·62 (4·68)	2·21 (2·24)	220
Id	Pale yellow	58·98 (59·23)	4·96 (4·97)	3·17 (3·29)	175
Ie	Pale yellow	56·82 (57·07)	4·87 (4·79)	3·03 (3·17)	208
If	Yellow	52·99 (53·10)	5·00 (5·09)	5·80 (5·90)	160
Ig	White	53·09 (53·63)	3·96 (3·80)	7·24 (7·22)	249
Ih	White	55·29 (55·46)	3·68 (3·66)	6·98 (6·93)	264
IIa	Yellow	56·68 (57·08)	4·79 (4·70)	3·41 (3·50)	255
IIb	Pale yellow	53·81 (54·28)	4·18 (4·29)	3·62 (3·72)	221
IIIa	Yellow	56·78 (57·08)	4·63 (4·79)	3·41 (3·50)	261
IIIb	Pale yellow	53·98 (54·28)	4·15 (4·29)	3·68 (3·72)	262
IVa	Yellow	57·21 (57·08)	4·67 (4·79)	3·41 (3·50)	212
IVb	Pale yellow	55·21 (54·28)	4·41 (4·29)	3·63 (3·72)	249
Vj	Pale yellow	50·45 (50·92)	5·39 (5·44)	7·28 (7·19)	131*
Vk	Pale yellow	49·53 (49·87)	4·45 (4·59)	7·41 (7·50)	170*
VIj	Pale yellow	51·27 (51·53)	5·42 (5·59)	7·17 (7·07)	140*
VIk	Pale yellow	51·15 (50·55)	4·69 (4·77)	7·49 (7·37)	135*

Expected values are in parentheses
All complexes decomposed except the ones with an asterisk

8·3(2H, *t*, $C^{17}H$), 8·6(2H, *d*, $C^{15}H$), ^{13}C NMR 22·8(C^6), 27·8(C^5), 30·4(C^7), 123·8(C^{12}), 123·9(C^{14}), 125·4(C^{18}), 127·2(C^4), 128·1(C^{13}), 130·1(C^{16} + C^{11}), 130·8(C^3), 132·4(C^2), 140·9(C^{17}), 144·4(C^{10}), 145·5(C^9), 150·3(C^{15}), 154·9(C^{19}), 159(C^1), 187·7(C^8). Similarly complex Ih was prepared using 1,10-phenanthroline (115 mg, 95%).

2.3f *Reaction of V with 2,2'-hexamethylenebipyridine*: The complex V (110 mg, 0·2 mmol) was stirred with 2,2'-hexamethylenebipyridine (48 mg, 0·2 mmol) in 5 ml of dichloromethane at room temperature for 3 h. The clear solution was concentrated and chromatographed on silica gel using dichloromethane–methanol (1%) as eluent. The



Scheme 1. Complexes: (I) $R = C_6H_5$; (II) $R = o\text{-}CH_3C_6H_4$; (III) $R = p\text{-}CH_3C_6H_4$; (IV) $R = C_6H_5CH_2$. (i) palladiumacetate in chloroform, room temperature; (ii) lithiumchloride in methanol, reflux.

pale yellow fraction is collected and evaporated. The complex Vk was recrystallised from dichloromethane/hexane (120 mg, 76%).

^{1}H NMR($CDCl_3$) 1·5(2H, *d*, $C^{16}H$), 1·95(2H, *m*, $C^{15}H$), 2·9(6H, *s*, C^8H), 3·5(2H, *m*, $C^{14}H$), 3·95(2H, *m*, C^7H), 5·75(1H, *d*, C^2H), 6·68(1H, *m*, C^3H), 6·95(2H, *m*, $C^{12}H + C^5H$), 7·17(1H, *t*, C^4H), 7·35(1H, *t*, $C^{10}H$), 7·70(1H, *t*, $C^{11}H$), 8·95(1H, *d*, C^9H), ^{13}C NMR 28·46(C^{16}), 29·25(C^{15}), 40·98(C^{14}), 52·58(C^8), 73·96(C^7), 121·54(C^3), 122·31(C^5), 122·31(C^5), 124·36(C^4), 125·16(C^{12}), 125·3(C^{10}), 131·85(C^2), 137·55(C^{11}), 147·15(C^6), 147·59(C^{13}), 152·61(C^9), 163·62(C^1). Similarly Vj was prepared using 2,2′-pentamethylenebipyridine (115 mg, 74%).

2.3g *Reaction of VI with 2,2′-hexamethylenebipyridine*: The complex VI (104 mg, 0·2 mmol) was stirred with 2,2′-hexamethylenebipyridine (48 mg, 0·2 mmol) in 5 ml of dichloromethane. The clear solution was concentrated and chromatographed on silica gel using dichloromethane–methanol (1%) as eluent. The pale yellow fraction is collected and evaporated. The complex VIk was recrystallised from dichloromethane/hexane (110 mg, 72%).

Table 2. Infrared spectral data (cm^{-1}).

Complex	ν_{COO-}	ν_{Pd-Cl}[b]	ν_{Pd-Cl}[t]	$\nu_{C=N}$	Others
Ia	1590, 1417				
Ib		270, 300		1587	
Ic			300	1600	
Id					1577, 1510
Ie					1606, 1507
If				1587	1504
Ig				1596	1086
Ih				1598	1086
IIa	1596, 1420				
IIb		265, 290		1593	
IIIa	1590, 1417				
IIIb		270, 300		1587	
IVa	1580, 1417			1603	
IVb		265, 290		1603	
Vj			290		
Vk			300		
VIj			300	1619	
VIk			310	1619	

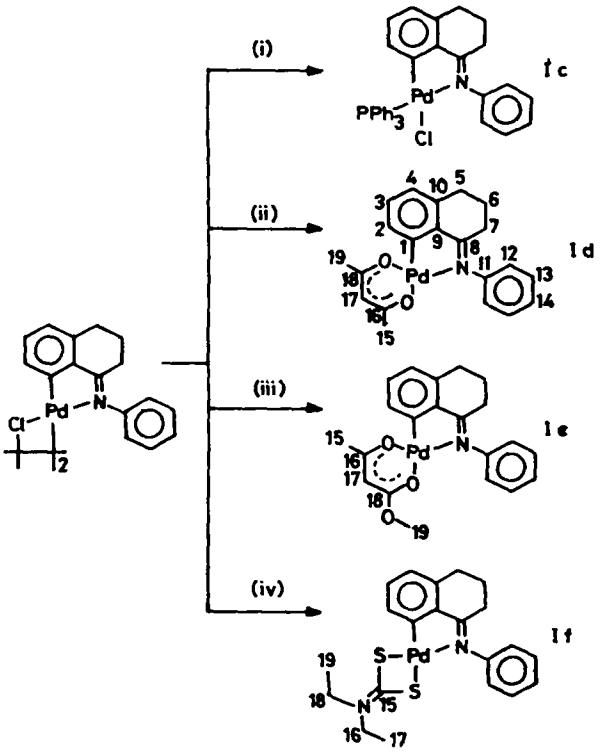
$\nu_{C=N}$ for ligands = 1632 cm^{-1}(I), 1629 cm^{-1}(II), 1629 cm^{-1}(III), and 1632 cm^{-1} (IV); [b]bridged Pd–Cl bond, [t]terminal Pd–Cl bond.

^{1}H NMR($CDCl_3$) 1·45(2H, *d*, C^{16}, H), 1·90(2H, *m*, C^{15}H), 3·40(2H, *t*, C^{14}H), 3·65(3H, *d*, C^8H), 5·85(1H, *d*, C^2H), 6·85(1H, *t*, C^4H), 7·0(1H, *t*, C^3H), 7·25(2H, *m*, C^5H + C^{12}H), 7·37(1H, *t*, C^{10}H), 7·75(1H, *t*, C^{11}H), 7·95(1H, *s*, C^7H), 8·9(1H, *d*, C^9H), ^{13}C NMR 28·2(C^{16}), 28·8(C^{15}), 40·5(C^{14}), 48·71(C^8), 122·48(C^3), 124·4(C^4), 125·35(C^{12}), 126·36(C^{10}), 130·1(C^5), 131·9(C^2), 137·8(C^{11}), 146·56(C^{13}), 152·19(C^9), 157·15(C^6), 163·76(C^1), 175·8(C^7). Similarly VIj was prepared using 2,2′-pentamethylene bipyridine (105 mg, 70%).

3. Results and discussion

Reaction between palladium(II)acetate and N-phenyl tetraloneketimine (I) in chloroform at room temperature gave acetatobridged dimeric compound $[Pd_2L_2(OAc)_2]$ (Ia). A series of similar type of complexes (IIa-IVa) were obtained from N-(*o*-methylphenyl)tetralone ketimine (II), N-(*p*-methylphenyl)tetraloneketimine (III) and N-benzyltetraloneketimine (IV) by the same method (scheme 1).

The acetato-bridged dimers exhibit two strong IR absorption bands corresponding to asymmetric and symmetric stretching frequencies of bridging acetato group at $\approx 1570\,cm^{-1}$ and $\approx 1420\,cm^{-1}$ respectively (Onoue and Moritani 1972). The corresponding chloro-bridged dimers, $[Pd_2L_2Cl_2]$ (Ib–IVb), were prepared from acetato-bridged complexes using LiCl in refluxing methanol. Acetato-bridged complexes are

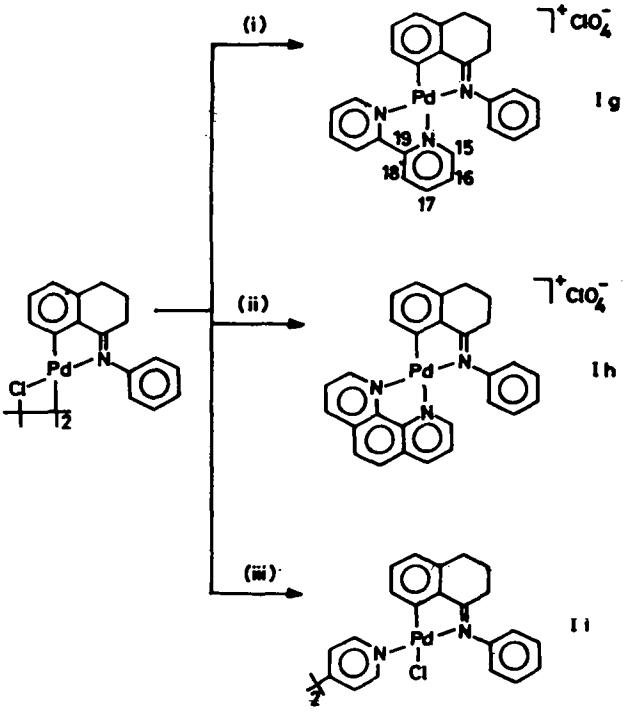


Scheme 2. (i) Triphenylphosphine in dichloromethane; (ii) acetylacetone and sodium in methanol; (iii) methylacetoacetate and KOH in methanol; (iv) sodium-diethyldithiocarbamate in methanol.

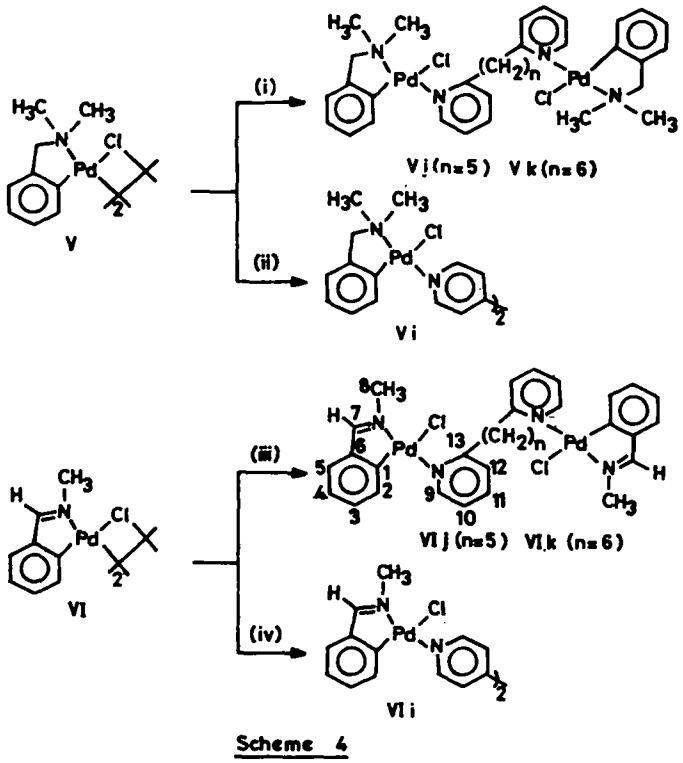
soluble in common organic solvents whereas chloro-bridged complexes are less soluble. The asymmetric stretching frequency of C=N bond in complexes is shifted to lower frequency of magnitude $\Delta\nu 10$–$40\,cm^{-1}$ (table 2) compared to the free ligand indicating that nitrogen is coordinated to the palladium through its lone pair of electrons (Onoue and Moritani 1972).

The methyl groups of bridging acetato groups appear as singlets in the ^1H NMR at $\approx 1{\cdot}4$ ppm, which represent an upfield shift compared to palladium acetate (2·04 ppm). This shift is due to the through-space shielding environment of the unmetallated phenyl ring (Vila *et al* 1986). Moreover the fact that the methyl groups of two bridging acetato groups are magnetically equivalent shows that the two Schiff bases are in a *trans* disposition. Two bridging Pd-Cl stretching frequencies for the chloro-bridged complexes also confirm the same configuration.

Chloro-bridged dimer Ib reacted with monodentate ligand like PPh_3 and yielded [PdL(PPh_3)Cl] (Ic), while with monoprotic bidentate ligands like acetylacetone, methylacetoacetate and diethyldithio-carbamate respectively it gave [PdL(acac)] (Id), [PdL(maa)] (Ie) and [PdL(dtc)] (If) (scheme 2). Complex Id shows two strong IR absorption bands at $1577\,cm^{-1}$ and $1510\,cm^{-1}$ for the chelated acetylacetato ligand. The ^1H NMR shows that the two methyl groups of acetylacetone ligand are not magnetically equivalent, appearing at 1·68 and 2·02 ppm. The enormous high field shift of one of the methyl groups is unprecedented in the cyclopalladated Schiff base complexes whereas it is found to be common in cyclopalladated heterocyclic ligands



Scheme 3. (i) $AgClO_4$ in acetonitrile, 2,2′-bipyridine in methanol; (ii) $AgClO_4$ in acetonitrile, 1,10-phenanthroline in methanol. (iii) 4,4′-bipyridine in methanol.



Scheme 4. (i) and (iii) Penta or hexamethylenebipyridine in dichloromethane. (ii) and (iv) 4,4′-bipyridine in methanol.

(Steel and Caygill 1987). This shift is due to through-space shielding of unmetallated phenyl ring. The complex Ie shows two strong IR absorption bands at 1606 cm^{-1} and 1507 cm^{-1} for chelated methylacetylacetato group (Nakamoto 1986). The diethyldithiocarbamate complex If shows one strong band at 1510 cm^{-1} corresponding to ν_{C-N}. ^1H NMR shows that the two ethyl groups of diethyldithiocarbamate are not magnetically equivalent (Constable 1985). Even at elevated temperature (60°C) there was no change in the spectrum suggesting double bond character of C–N bond.

Bridge-splitting reactions of Ib with neutral bidentate ligands have also been carried out. The complex Ib reacted with 2,2′-bipyridine and 1,10-phenanthroline in the presence of $AgClO_4$ giving cationic complexes of the type $[PdL(N-N)]^+ClO_4^-$. (N–N = 2,2′-bipyridine Ig and 1,10-phenanthroline Ih) (scheme 3). The IR spectra of Ig and Ih show a strong ν_{Cl-O} band at 1086 cm^{-1} (Nakamoto 1986).

Reaction of 2,2′-bipyridine with Ib gave cationic complex Ig where both nitrogen atoms are coordinated with same metal atom. We extended this type of reaction with 4,4′-bipyridine in order to get monometallated binuclear complexes of the type Ii, Vi and VIi from Ib, di-μ-chloro*bis*[N,N-dimethylbenzylamine C^2,N]dipalladium(II) (V) and di-μ-cholor*obis*[N-benzylidene methylamine C^2,N]dipalladium (II) (VI) respectively (schemes 3 and 4). Since the solubility of the complexes Ii, Vi and VIi was poor in organic solvents we were not able to characterise these complexes completely. To enhance the solubility of monometallated binuclear complexes we used 2,2′-penta and

hexamethylenebipyridine as bridge-splitting ligands instead of 4,4′-bipyridine. The complexes obtained from V (Vj $n = 5$, Vk $n = 6$) and VI (VIj $n = 5$, VIk $n = 6$) using the above ligands were highly soluble in common organic solvents (scheme 4). Our attempt to prepare the monometallated binuclear complex using 2,2′-penta and hexamethylenebipyridine from Ib was not successful. The structures of all complexes are unequivocally assigned by ^{1}H NMR and ^{13}C NMR spectroscopy. The ^{13}C resonance of palladated carbon atom typically appears around 160 ppm in all complexes. This corresponds to a low field shift of about 40 ppm compared to the chemical shift of the free ligand (Klaus and Rys 1981). ^{1}H NMR spectra of the monometallated binuclear complexes Vj, Vk, VIj and VIk shows that the proton adjacent to the metallated carbon atom is shielded due to the anisotropic shielding effect of the pyridine ring (Trofimenko 1973; Chakladar *et al* 1992).

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References

Bose A and Saha C A 1989 *J. Mol. Catal.* **49** 271
Bruce D W 1993 *J. Chem. Soc., Dalton Trans.* 2983
Chakladar S, Paul P, Mukherjee A K, Dutta S K, Nanda K K, Podder D and Nag K 1992 *J. Chem. Soc., Dalton Trans.* 3119
Constable E C, 1984 *Polyhedron* **3** 1037
Constable E C 1985 *J. Chem. Soc., Dalton Trans.* 1719
Cope A C and Friedrich E C 1968 *J. Am. Chem. Soc.* **90** 909
Hugentobler M, Klaus A J, Mettler H, Rys P and Wehrle G 1982 *Helv. Chim. Acta* **65** 1202
Jampolsky L M, Baum M, Kaiser S, Sternbach L H and Goldberg M N 1952 *J. Am. Chem. Soc.* **74** 5222
Klaus A J and Rys P 1981 *Helv. Chim. Acta* **64** 1452
Nakamoto K 1986 *IR and Raman spectra of inorganic and coordination compounds* 4th edn (New York: Wiley Interscience)
Newkome G R, Kohli D K and Fronczek F P 1982 *J. Am. Chem. Soc.* **104** 994
Newkome G R, Puckett W E, Gupta V K and Kiefer G E 1986 *Chem. Rev.* **86** 451
Nielson A J 1981 *J. Chem. Soc. Dalton Trans.* 205
Onoue H and Moritani I 1972 *J. Organomet. Chem.* **43** 431
Perrin D D and Armarego W L F 1988 *Purification of laboratory chemicals.* 3rd edn (Oxford: Pergamon)
Phillips I G and Steel P J 1991 *J. Organomet. Chem.* **410** 247
Ryabov A D 1985 *Synthesis* 233
Ryabov A D 1990 *Chem. Rev.* **90** 403
Sokolov V I 1983 *Pure Appl. Chem.* **55** 1837
Steel P J and Caygill G B 1987 *J. Organomet. Chem.* **327** 101
Stephenson T A, Morehouse S M, Powell A R, Heffer J P and Wilkinson G 1965 *J. Chem. Soc.* 3632
Trofimenko S 1973 *Inorg. Chem.* **12** 1215
Vila J M, Pereira M T, Gayoso E and Gayaso M 1986 *Transition Met. Chem.* **11** 342
Vila J M, Gayoso M, Pereira M T, Ortigueira J M, Fernandez A, Bailey N A and Adams H 1993 *Polyhedron* **12** 171
Wakatsuki Y, Yamazaki H, Grutsch P A, Santhanam M and Kutal C 1985 *J. Am. Chem. Soc.* **107** 8153