Journal of Organometallic Chemistry, 54 (1973) 391–397
© Elsevier Sequoia S.A., Lausanne – Printed in the Netherlands

(*N*,*N*-DIMETHYLBENZYLAMINE-2-*C*,*N*)PALLADIUM(II) AND -PLATINUM(II) COMPLEXES CONTAINING *N*-SUBSTITUTED SALICYLALDIMINES

B. E. REICHERT and B. O. WEST
Department of Chemistry, Monash University, Clayton, Victoria 3168 (*Australia*)

(Received October 10th, 1972)

SUMMARY

Reactions of the thallium(I) derivatives of alkyl and aryl salicylaldimines, TlSal=N–R, and the quadridentate Schiff base *N*,*N*′-ethylenebis(salicylaldimine), Tl_2-Salen, with [(*N*,*N* dimethylbenzylamine-2-*C*,*N*) MCl]$_2$ ([(DmbaMCl]$_2$; M = Pd, Pt) give the complexes DmbaMSal=N–R and [DmbaM]$_2$Salen. The ^{1}H NMR spectra show them to have two coordinated nitrogen atoms *trans*. $^3J(^{195}Pt–^1H)$ has been measured for a number of protons in the platinum derivatives.

INTRODUCTION

Previous reports of Pd and Pt organometallic compounds containing *N*-substituted salicylaldimines have described allyl–Pd^{II}L[1] and $(CH_3)_3Pt^{IV}L$ derivatives[2] where L is the anion of the appropriate Schiff base. This paper describes the synthesis of a series of stable Pd^{II} and Pt^{II} complexes containing various *N*-substituted salicylaldimines together with a chelating organometallic group derived from *N*,*N*-dimethylbenzylamine in which a metal–carbon σ bond exists between a metal and the 2-carbon atom of the aromatic ring (Fig. 1).

The ^{1}H NMR spectra of these complexes has enabled their structures to be deduced because of the influence of the magnetic anisotropy of *N*-aryl substituents on the Schiff base ligands.

In addition it has been possible to measure $^{195}Pt–^1H$ coupling constants in which interaction is occurring through three bonds.

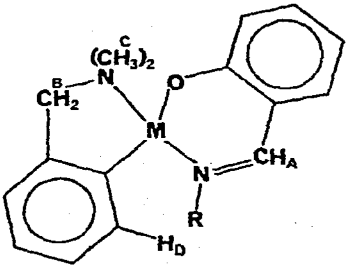

Fig. 1.

RESULTS AND DISCUSSION

Syntheses

The complexes (*N*,*N*-dimethylbenzylamine-2-*C*,*N*)-MSal=N–R [DmbaMSal=N–R; Sal=N–R substituted salicylaldiminato anion] where M = Pd, Pt and R = CH_3, C_2H_5, C_6H_{11}, C_6H_5, *p*-ClC_6H_4 have been synthesized by the reaction of the chlorobridged dimers[3] $[DmbaMCl]_2$ with the thallium(I) salts of the Schiff bases[4] in dichloromethane. After filtration of the precipitated thallium(I) chloride the products were isolated by the addition of hexane and partial evaporation of the solution. The quadridentate Schiff base *N*,*N'*-ethylenebis(salicylaldimine) (H_2Salen) gives the binuclear complexes $[DmbaM]_2$Salen (M = Pd, Pt) by the analogous reactions using Tl_2Salen[4]. In these latter compounds the ligand is expected to behave as a bridging ligand bidentate on each of two metal atoms, as has previously been suggested for some complexes of rhodium[5], iridium[5] and palladium[1]. The palladium complexes of the Schiff bases HSal=N–C_6H_5, HSal=N–*p*-ClC_6H_4 and H_2Salen were also prepared by reaction of $[DmbaPdCl]_2$ with the free Schiff base and triethylamine in acetone. [The simple *N*-alkyl salicylaldimines are liquids and much more readily handled as the thallium(I) salts.] This method, however, proved less successful for the platinum complexes, 70% of the starting material being recovered after 24 h reaction.

The palladium derivatives are all yellow and the platinum derivatives of the alkyl salicylaldimines and Salen, yellow-orange. The compound DmbaPtSal=N–*p*-ClC_6H_4 is orange-red, while DmbaPtSal=N–C_6H_5 exists in two crystal forms, orange-red and orange-yellow. A preliminary X-ray diffraction study[6] has indicated that the red form is monoclinic with space group $P2_1$ or $P2_1/m$ having two molecules per unit cell.

It is considered that the molecules represented by Fig. 1 would not possess a mirror plane, a requirement for $P2_1/m$ and therefore the space group would be $P2_1$. This in turn indicates that all the molecules in a single crystal should be of one enantiomeric form. The yellow crystals, on the other hand, have the tetragonal space group $I4_1/a$ with 16 molecules per unit cell and presumably are crystal racemates. A complete structural determination for this compound is currently in progress in this department.

Spectra and structure

The ^1H NMR spectra of the compounds are shown in Table 1, with the numbering of protons referring to Fig. 1, which shows the expected structure. In the Salen complexes two such units are connected by a CH_2CH_2 bridge in place of R. An interesting feature of the spectra which has enabled assignment of the structure shown in Fig. 1 with the nitrogen atoms *trans*, rather than the alternative structure with *cis* nitrogen atoms, is the appearance of a doublet 0.5 to 0.6 ppm upfield of the remainder of the aromatic proton resonances when R is an aryl group. A comparison of the aromatic regions in the ^1H NMR spectra of DmbaPdSal=N–R with R = phenyl and cyclohexyl is shown in Fig. 2. This doublet has a separation of approximately 8 Hz, a typical *ortho* coupling for aromatic protons, and is assigned to the proton H_D which has been shifted upfield in the cases where R is aryl by the anisotropic shielding due to the ring current of the adjacent benzene ring. If the nitrogen

TABLE 1

^{1}H NMR SPECTRA[a]

Complex	*δ Values (ppm downfield from internal TMS)*				
	Aromatic	H_A	H_B	H_C	R[b]
DmbaPdSal=N–R					
R=CH_3	7.25–6.32	7.67	3.92	2.65	CH_3 3.68d[c]
C_2H_5	7.31–6.32	7.70	3.92	2.65	CH_2 3.85q[d] CH_3 1.32t[d]
C_6H_{11}	7.23–6.32	7.74	3.90	2.66	C_6H_{11} 4.2–1.1
C_6H_5	7.46–5.71	7.97	3.93	2.75	Aromatic
p-ClC_6H_4	7.41–5.74	7.90	3.93	2.73	Aromatic
[DmbaPd]$_2$Salen	7.15–6.23	7.54	3.55	2.43	CH_2 4.24
DmbaPtSal=N–R					
R=CH_3	7.49–6.35	7.77	3.96	2.75	CH_3 3.92d[e]
C_2H_5	7.35–6.34	7.78	3.95	2.75	CH_2 4.10q[f] CH_3 1.33t[f]
C_6H_{11}	7.33–6.34	7.81	3.93	2.76	C_6H_{11} 4.4–1.1
C_6H_5	7.46–5.62	8.11	3.95	2.84	Aromatic
p-ClC_6H_4	7.47–5.67	8.04	3.95	2.82	Aromatic
[DmbaPt]$_2$Salen[g]	7.27–6.35	7.60	3.70	2.57	CH_2 4.46

[a] In deuterochloroform. [b] d=Doublet, t=triplet, q=quadruplet. [c] $J(CH_3–H_A)$ 1.3 Hz. [d] $J(CH_2–CH_3)$ 7.3 Hz. [e] $J(CH_3–H_A)$ 1.1 Hz. [f] $J(CH_2–CH_3)$ 7.2 Hz. [g] Time-averaged spectrum obtained because of low solubility.

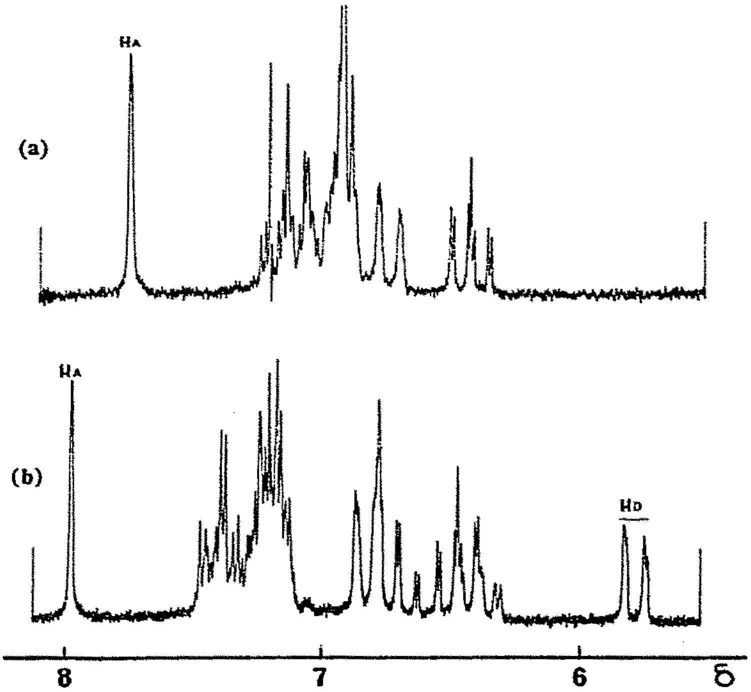

Fig. 2. ^{1}H NMR spectra in the aromatic region for: (a), DmbaPdSal=N–C_6H_{11}; (b), DmbaPdSal=N–C_6H_5.

atoms were *cis* the aromatic protons would be essentially unaffected and the methyl protons H_C shifted upfield instead, which does not occur, implying the structure shown. This use of the anisotropy of an aromatic ring has recently been used to help assign the structure of other organometallic compounds[1,7,8] and appears to be a useful technique particularly well suited to the investigation of structures of metal Schiff base chelates, where a shielding group can easily be built into the molecule.

As the effect of a metal–carbon σ-bond on the coordination of a Schiff base in a square planar complex has not previously been observed and would be difficult to predict, the stereochemistry of these complexes is interesting in demonstrating the preferred coordination of the salicylaldimine with the oxygen *trans* to the metal–carbon bond.

Satellites due to ^{195}Pt ($I=\frac{1}{2}$, natural abundance 33.8%) can be observed for a number of resonances in the ^{1}H NMR spectra of the platinum derivatives enabling the measurement of several coupling constants through three bonds between ^{195}Pt and ^{1}H. These values are shown in Table 2. In the compound $[\text{DmbaPtCl}]_2$, the reported[3] coupling constants are $^3J(\text{Pt–H}_B)$ 55 and $^3J(\text{Pt–H}_C)$ 48 Hz, values which are appreciably higher than those found in the complexes studied here. The reduced coupling constant in these complexes is presumably due to the coordination of the dimethylbenzylamine nitrogen being weakened by the more strongly coordinating Schiff base. Hence the value of this coupling constant may be useful as a measure of the *trans* effect of a ligand opposite the nitrogen atom in (*N*,*N*-dimethylbenzylamine-2-*C*,*N*)platinum complexes. The increase in these couplings when R changes from alkyl to the less electropositive aryl groups is consistent with this.

It has been possible to measure $^3J(\text{Pt–H}_D)$ only in the two cases with R= C_6H_5 and *p*-ClC_6H_4 where the resonance due to H_D is separated from the remainder of the aromatic region, enabling the ^{195}Pt satellites to be observed. The only previous measurement of a coupling constant with the *ortho* proton of an aryl group σ-bonded to platinum has been in a derivative of di-tert-butyl-*p*-tolylphosphine[9], the value of ^3J(Pt–H) in that case being 66.6 Hz. Again this is considerably higher than the values observed here and this may again be due to the difference in the substituent *trans* to the platinum–carbon bond, being chloride in the phosphine compound and the oxygen of a salicylaldimine in our complexes.

TABLE 2

^{195}Pt–^{1}H COUPLING CONSTANTS

Complex	*$^3J(^{195}Pt–^1H)$ values (Hz)*				
	H_A	*H_B*	*H_C*	*H_D*	*R*
Dmba Pt Sal=N–R					
R=CH_3	81.6	41.5	33.3		CH_3 42.1
C_2H_5	82.3	41.7	33.0		CH_2 47.7
C_6H_{11}	87.3	41.9	33.0		
C_6H_5	78.4	44.4	34.9	41.4	
p-ClC_6H_4	77.3	44.6	35.2	41.8	
$[DmbaPt]_2Salen$	83.6	42	32.8		CH_2 50

The values given for the couplings with protons of the salicylaldimine are the first examples of Pt–H couplings in Schiff base complexes, so no comparison may be made with other compounds. Although the values may be regarded as giving a typical order of magnitude to be expected for the couplings in platinum Schiff base chelates they are expected to be sensitive to the substituent *trans* to the imine nitrogen. It can be seen that $^3J(\text{Pt–H}_A)$ shows considerable variation with R, probably caused by the influence of R both on strength of coordination and electron density in the C=N bond. It is also noteworthy that the magnitude of $^3J(\text{Pt–H}_A)$ is comparable in magnitude to $^2J(\text{Pt–H})$ in methyl platinum compounds[10] which, although it may show considerable variation with different *trans* substituents[11], does not have any values appreciably higher than those found here for a coupling through three bonds.

The infrared spectra (KBr disc) of the compounds in the region 1700–1100 cm^{-1} where the C=N, C=C, C–H, C–O and C–N vibrations of Schiff bases occur are typical of metal salicylaldimine chelates. The spectra are complicated by the presence of bands in this region due to the Dmba entity as shown in the starting materials $[\text{DmbaMCl}]_2$.

The mass spectra of the bidentate salicylaldimine complexes DmbaMSal=N–R all display the parent ion with the expected pattern for the isotopes of the metal. Doubly charged parent ions are also shown. Peaks corresponding to the ions $\text{CH}_3\text{C}_6\text{H}_4\text{MSal=N–R}^+$, $\text{CH}_3\text{C}_6\text{H}_4\text{M}^+$, $[(\text{MSal=N–R})-\text{H}]^+$, Sal=N–R^+, $\text{C}_6\text{H}_4\text{CH}_2\text{N(CH}_3)_2^+$ and $\text{CH}_3\text{C}_6\text{H}_4^+$ are apparent for all the complexes while those of the aryl salicylaldimines also give R^+. The binuclear compounds $[\text{DmbaM}]_2\text{Salen}$ do not give mass spectra showing the parent ion.

EXPERIMENTAL

Instrumentation

^{1}H NMR spectra were measured with a Varian Associates HA-100 spectrometer using a Varian computer for time averaging. Infrared spectra were recorded on a Perkin–Elmer 521 spectrophotometer. The mass spectra were obtained with a Hitachi–Perkin–Elmer RMU-6E instrument using an ion chamber temperature of 200° and an electron energy of 70 eV. Solution molecular weights were determined with a Mechrolab Model 301A osmometer.

X-ray crystallographic data was obtained from Weissenberg and precession photographs using Cu-K_α and Mo-K_α radiation.

Starting materials

The palladium and platinum compounds $[\text{DmbaMCl}]_2$ were obtained by the literature method[3]. The thallium(I) salts of the Schiff bases were prepared by reaction of the free salicylaldimine with thallium(I) ethoxide[4].

Syntheses

The mononuclear bidentate complexes are extremely soluble in chloroform and dichloromethane, readily soluble in acetone but almost insoluble in hexane, while the Salen complexes are somewhat less soluble, particularly in the case of platinum. All the complexes are stable to the atmosphere and quite stable thermally, although they do not give sharp melting points, decomposing while melting over a temperature range.

DmbaMSal=N–R ($M=Pd$, Pt; $R=CH_3$, C_2H_5, C_6H_{11}, C_6H_5, p-ClC_6H_4) and $[DmbaM]_2$Salen ($M=Pd$, Pt). $[DmbaMCl]_2$ was dissolved in dichloromethane, treated with a slight excess (3–4%) of the appropriate thallium(I) Schiff base compound, and left stirring overnight. The thallium(I) chloride was filtered off (this frequently presented a problem, particularly in the platinum reactions where a sterilizing filter pad was used), hexane added, and the solution reduced in volume under reduced pressure until crystallization occurred. The platinum derivatives generally crystallized with difficulty and were obtained in lower yield. Analytical figures, molecular weights and yields for the compounds are given in Table 3.

Reaction of $[DmbaPdCl]_2$ with free Schiff bases and triethylamine. $[DmbaPdCl]_2$ was suspended in acetone and treated with a small excess of HSal=N–R ($R=C_6H_5$, p-ClC_6H_4) or H_2Salen and triethylamine (as a 1% solution in ethanol). After stirring overnight the starting material had dissolved in the cases of the bidentate ligands, whereas in the reaction with H_2Salen a large quantity of yellow solid, different in appearance to $[DmbaPdCl]_2$, had separated. Water was added, the volume and products which separated filtered off and recrystallized from dichloromethane/

TABLE 3

ANALYTICAL DATA, MOLECULAR WEIGHTS AND YIELDS

Complex	*Formula*	*Analyses found (calcd.) (%)*				*Mol. wt. (m/e)*[a] *found (calcd.)*	*Yield (%)*
		C	*H*	*N*	*Cl*		
DmbaPdSal=N–R							
$R=CH_3$	$C_{17}H_{20}N_2OPd$	54.43 (54.48)	5.48 (5.38)	7.36 (7.48)		374 (374)	70
C_2H_5	$C_{18}H_{22}N_2OPd$	55.88 (55.61)	5.56 (5.70)	7.11 (7.21)		388 (388)	75
C_6H_{11}	$C_{22}H_{28}N_2OPd$	59.59 (59.66)	6.65 (6.37)	6.31 (6.33)		442 (442)	81
C_6H_5	$C_{22}H_{22}N_2OPd$	60.51 (60.49)	5.07 (5.08)	6.24 (6.41)		336 (336)	92
p-ClC_6H_4	$C_{22}H_{21}N_2ClOPd$	55.84 (56.07)	4.34 (4.49)	5.74 (5.94)	7.6 (7.5)	470 (470)	84
$[DmbaPd]_2$*Salen*	$C_{34}H_{38}N_4O_2Pd_2$	54.22 (54.63)	5.01 (5.12)	7.58 (7.50)		716[b] (747.5)[c]	93
DmbaPtSal=N–R							
$R=CH_3$	$C_{17}H_{20}N_2OPt$	44.10 (44.06)	4.29 (4.35)	6.06 (6.04)		463 (463)	46
C_2H_5	$C_{18}H_{22}N_2OPt$	44.99 (45.28)	4.61 (4.64)	5.57 (5.87)		477 (477)	51
C_6H_{11}	$C_{22}H_{28}N_2OPt$	49.21 (49.71)	5.41 (5.31)	5.20 (5.27)		531 (531)	51
C_6H_5	$C_{22}H_{22}N_2OPt$	50.13 (50.28)	4.38 (4.22)	5.00 (5.33)		525 (525)	43
p-ClC_6H_4	$C_{22}H_{21}N_2ClOPt$	47.04 (47.19)	3.88 (3.78)	4.95 (5.00)	6.2 (6.3)	559 (559)	62
$[DmbaPt]_2$*Salen*	$C_{34}H_{38}N_4O_2Pt_2$	43.85 (44.15)	4.12 (4.14)	5.72 (6.06)		900[b] (924.9)[c]	67

[a] Mass spectrometric, for ^{106}Pd or ^{195}Pt. [b] Osmometric in $CHCl_3$ solution. [c] From standard atomic weights.

hexane. The identity of the products as DmbaPdSal=N–R ($R = C_6H_5$, p-ClC_6H_4) and $[DmbaPd]_2$Salen was confirmed by infrared spectra and elemental analyses. Yields were 62%, 80% and 44%, respectively.

Reaction of $[DmbaPtCl]_2$ *with* HSal=N–C_6H_5 *and triethylamine.* $[DmbaPtCl]_2$ was suspended in acetone and treated with a small excess of HSal=N–C_6H_5 and triethylamine (1% in ethanol). After stirring for 24 h 70% of the $[DmbaPtCl]_2$ was recovered unchanged and only a 6% yield of impure product could be isolated.

ACKNOWLEDGEMENT

We wish to thank Mr. I. Willing of C.S.I.R.O. for obtaining the time-averaged NMR spectrum, and Mr. B. K. Miskin of this department for the X-ray data.

REFERENCES

1 B. E. Reichert and B. O. West. *J. Organometal. Chem.*, 36 (1972) C29.
2 V. Romano, R. Badalamenti, T. Pizzino and F. Maggio *J. Organometal. Chem.*, 42 (1972) 199.
3 A. C. Cope and E. C. Friedrich, *J. Amer. Chem. Soc.*, 90 (1968) 909.
4 R. J. Cozens, K. S. Murray and B. O. West, *Aust. J. Chem.*, 23 (1970) 683.
5 R. J. Cozens, K. S. Murray and B. O. West, *J. Organometal. Chem.*, 27 (1971) 399.
6 B.K. Miskin, private communication.
7 J. W. Faller and A. J. Jakubowski, *J. Organometal. Chem.*, 31 (1971) C75.
8 A. Musco, R. Rampone, P. Ganis and C. Pedone, *J. Organometal. Chem.*, 34 (1972) C48.
9 A. J. Cheney, B. E. Mann, B. L. Shaw and R. M. Slade, *Chem. Commun.*, (1970) 1176.
10 J. S. Thayer, *Organometal. Chem. Rev. Sect. A*, 5 (1970) 53.
11 J. D. Ruddick and B. L. Shaw, *Chem. Commun.*, (1967) 1135.