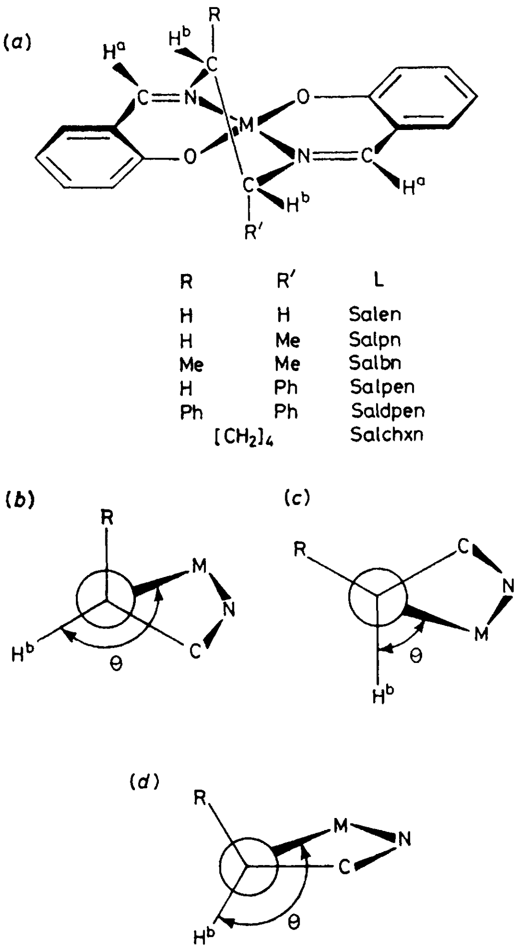
Optically Active Complexes of Schiff Bases. Part 6.[1] Palladium(II) and Platinum(II) Complexes with Quadridentate Schiff Bases of Salicylaldehyde

By **Edoardo Cesarotti, Alessandro Pasini,** and **Renato Ugo,*** Istituto di Chimica Generale e Inorganica dell'Università Centro C.N.R., Via Venezian 21, 20133 Milano, Italy

The synthesis and properties of palladium(II) and platinum(II) complexes with quadridentate Schiff bases derived from the condensation of salicylaldehyde and (*R*)-1,2-diamines are described. The ligand conformation of the platinum(II) complexes is discussed on the basis of the circular dichroism and the ^1H n.m.r. spectra. The anomalous patterns of the circular dichroism spectra of palladium(II) derivatives are also reported.

COMPLEXES of quadridentate Schiff bases H_2L, derived from the condensation of 2 mol of salicylaldehyde with 1 mol of an optically active 1,2-diamine (Figure 1), are known for a variety of metal ions; with first-row transition metals their chemical, conformational, and, in some cases, catalytic properties have been widely studied.[1-6] However, little is known even from the synthetic point of view on the related complexes with the platinum metals; a palladium(II) derivative of ethylenediamine (en)[7] has been reported, and polymeric complexes of quadridentate Schiff bases with both palladium(II) and platinum(II) have been described.[8]



R	R'	L
H	H	Salen
H	Me	Salpn
Me	Me	Salbn
H	Ph	Salpen
Ph	Ph	Saldpen
[CH₂]₄		Salchxn

FIGURE 1 Schematic drawing of the complexes in the axial conformation (*a*). The chiral diamines used are all in the (*R*) or (*R*,*R*) absolute configuration. Newman projections of the C–N bond of the diamine in the '*gauche*' axial (*b*), '*gauche*' equatorial (*c*), and 'envelope' (*d*) conformations of the diamine chelate ring

In the course of our studies on metal complexes with optically active Schiff bases, we have become interested in platinum(II) and palladium(II) complexes, since these latter are known to display some interesting properties as hydrogenation catalysts.[7] We have extended and confirmed the hydrogenation catalytic properties for a series of palladium(II) complexes with the quadridentate Schiff bases described in this paper; the related platinum(II) complexes show a much lower catalytic activity. We will report on these catalytic studies elsewhere.[9] Failure to achieve asymmetric hydrogenation of prochiral olefins with the palladium(II) complexes prompted us to investigate in detail the conformational aspects of these complexes, in parallel with those of the related platinum(II) compounds. Abbreviations for the diamines are given in the caption to Figure 1.

RESULTS AND DISCUSSION

The complexes [ML] were (L = a quadridentate salicylideneiminate) were prepared *via* routes (i)—(iv) (see Experimental section) where HOC_6H_4CHO = salicylaldehyde, R = CH_3 for M = Pt^{II}, and R = C_6H_5

$$M[NO_3]_2 + H_2L \longrightarrow [ML] + 2HNO_3 \quad \text{(i)}$$

$$[M(OC_6H_4CHO)_2] + \text{diamine} \longrightarrow [ML] \quad \text{(ii)}$$

$$cis\text{-}[MCl_2(NCR)_2] + Tl_2[L] \longrightarrow [ML] + 2TlCl + 2RCN \quad \text{(iii)}$$

$$[M(\text{diamine})Cl_2] + 2Tl[OC_6H_4CHO] \longrightarrow [ML] + 2TlCl \quad \text{(iv)}$$

for M = Pd^{II}. Routes (i) and (ii) were used for palladium(II) complexes starting from an alcoholic solution of freshly prepared $Pd[NO_3]_2\cdot nH_2O$[7] or $[Pd(OC_6H_4CHO)_2]$[10] since simple non-polymeric salts of the type MX_2 are not easily available (M = Pd or Pt, X = halide). The analogous platinum reagents $Pt[NO_3]_2\cdot nH_2O$ and $[Pt(OC_6H_4CHO)_2]$ are not readily available. Attempts to use $K_2[MCl_4]$ (M = Pt or Pd) as starting materials gave poor results, although these compounds were used to prepare platinum and palladium complexes with quadridentate Schiff bases bound to a polymer.[8]

Routes (iii) and (iv) were successful for both palladium(II) and platinum(II) ions, although for the latter, only route (iv) gave reasonably high yields of pure products.

Platinum Complexes.—The platinum derivatives, crystallized from chloroform, were found to contain, in the solid state, variable amounts of solvent molecules (Table 1) which probably interact with the phenolic oxygen atoms, as in some $CHCl_3$ adducts of related complexes *e.g.* [Co(salen)] [11] and [Cu(salen)].[12] The solvent molecules could only be removed by heating the compounds *in vacuo*. The presence of chloroform is confirmed by the appearance of a resonance at δ 8.3 p.p.m. relative to $SiMe_4$ in the ^1H n.m.r. spectra recorded in dimethylformamide (dmf) or dimethyl sulphoxide (dmso) solutions. Thermogravimetric analysis shows that the loss of chloroform takes place slowly over a large temperature range. No adducts of this type have been obtained from dmf.

TABLE 1

Analytical data

Complex	Analysis (%) [a] C	H	N	*M* [b]
[Pt(salen)]	41.6 (41.5)	3.0 (3.0)	6.0 (6.1)	
[Pt{sal(−)pn}]·0.67 $CHCl_3$	38.0 (38.3)	2.9 (3.0)	5.0 (5.1)	
[Pt{sal(−)bn}]·0.5 $CHCl_3$	40.7 (40.5)	3.5 (3.4)	5.2 (5.1)	
[Pt{sal(*m*)bn}]·0.33 $CHCl_3$	41.1 (41.7)	3.5 (3.4)	5.6 (5.3)	
[Pt{sal(+)dpen}]	54.0 (54.8)	3.5 (3.6)	4.5 (4.6)	
[Pt{sal(*m*)dpen}]	54.2 (54.8)	3.8 (3.6)	4.4 (4.6)	
[Pt{sal(−)pen}]·0.5$CHCl_3$	45.8 (45.2)	3.3 (3.1)	4.3 (4.7)	
[Pt{sal(−)chxn}]·0.5$CHCl_3$	42.4 (42.4)	3.9 (3.6)	5.2 (4.9)	
[Pd(salen)]	51.7 (51.6)	4.0 (4.3)	7.6 (7.5)	
[Pd{sal(−)pn}]	52.8 (52.8)	4.0 (4.2)	7.5 (7.3)	370 (386.4)
[Pd{sal(−)bn}]	54.1 (54.0)	4.5 (4.5)	6.9 (7.0)	395 (400.4)
[Pd{sal(*m*)bn}]	53.8 (54.0)	4.3 (4.5)	7.2 (7.0)	410 (400.4)
[Pd{sal(+)dpen}]	63.4 (64.0)	4.2 (4.2)	5.6 (5.4)	540 (524.4)
[Pd{sal(*m*)dpen}]	64.8 (64.0)	4.0 (4.2)	5.1 (5.4)	510 (524.4)
[Pd{sal(−)pen}]	58.3 (58.9)	4.2 (4.0)	6.0 (6.2)	
[Pd{sal(−)chxn}]	56.4 (56.3)	4.7 (4.7)	6.5 (6.6)	
[Pd{sal(*m*)chxn}]	55.8 (56.3)	4.6 (4.7)	6.4 (6.6)	

[a] Calculated values are given in parentheses. [b] In chloroform solutions.

The circular dichroism (c.d.) spectra of [Pt{(*R*)-L}] are shown in Figure 2. The electronic origin of some features of these spectra has already been discussed,[3,6] in particular the Cotton effects around 350 nm were attributed to the π→π* transitions essentially localized on the azomethine chromophores. These transitions usually give rise in the c.d. spectra to two bands of different sign caused by the exciton interaction of the transitions of the two azomethine groups, which are not coplanar in complexes of chiral diamines [3] [Figure 1(*a*)]. The sign of such a positive–negative splitting can therefore be correlated to the conformation (axial *vs.* equatorial substituents) of the five-membered chelate ring.[3,6] This splitting cannot be detected in complexes of Ni^{II}, Pd^{II}, and Pt^{II}, because of the overlapping with other transitions (see Figures 2—4).[3,6] However, the trends of the

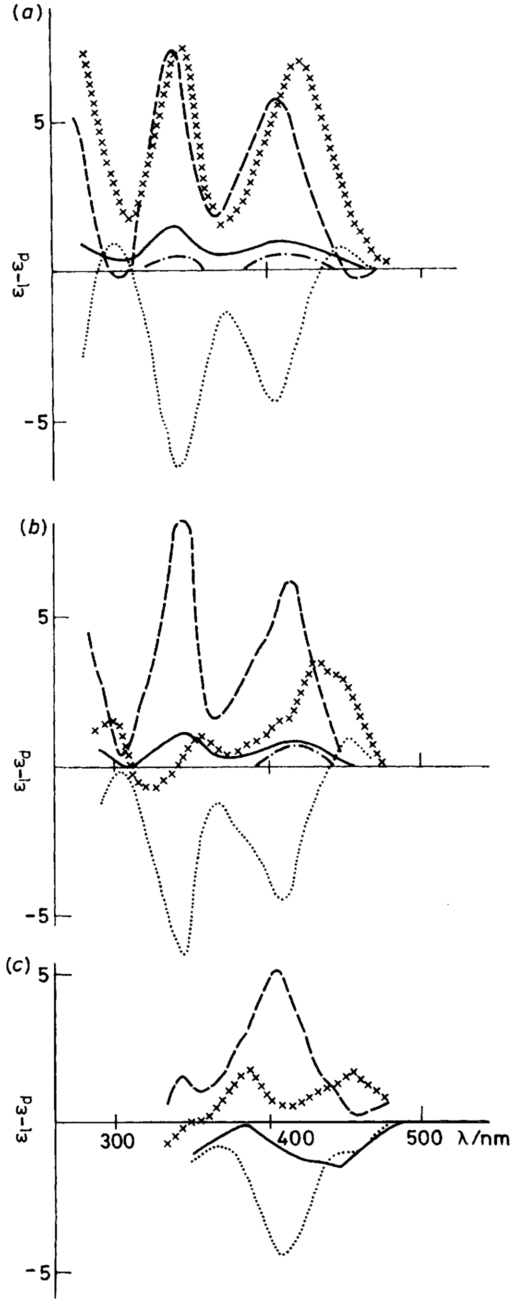


FIGURE 2 Circular dichroism spectra, in dmf solution (*a*), in chloroform solution (*b*), and in the solid state (*c*, KBr pellets, arbitrary units) of [Pt{sal(−)pn}] (——); [Pt{sal(−)bn}] (— — —); [Pt{sal(−)pen}] (— · — · —); [Pt{sal(+)dpen}] (× × ×); and [Pt{sal(−)chxn}] (· · · ·). Units for $\varepsilon_l - \varepsilon_d$ are $dm^3 mol^{-1} cm^{-1}$

spectra can be used to infer the conformation of the complex by comparison with the spectrum of the cyclohexanediamine derivative which always has equatorial substituents.

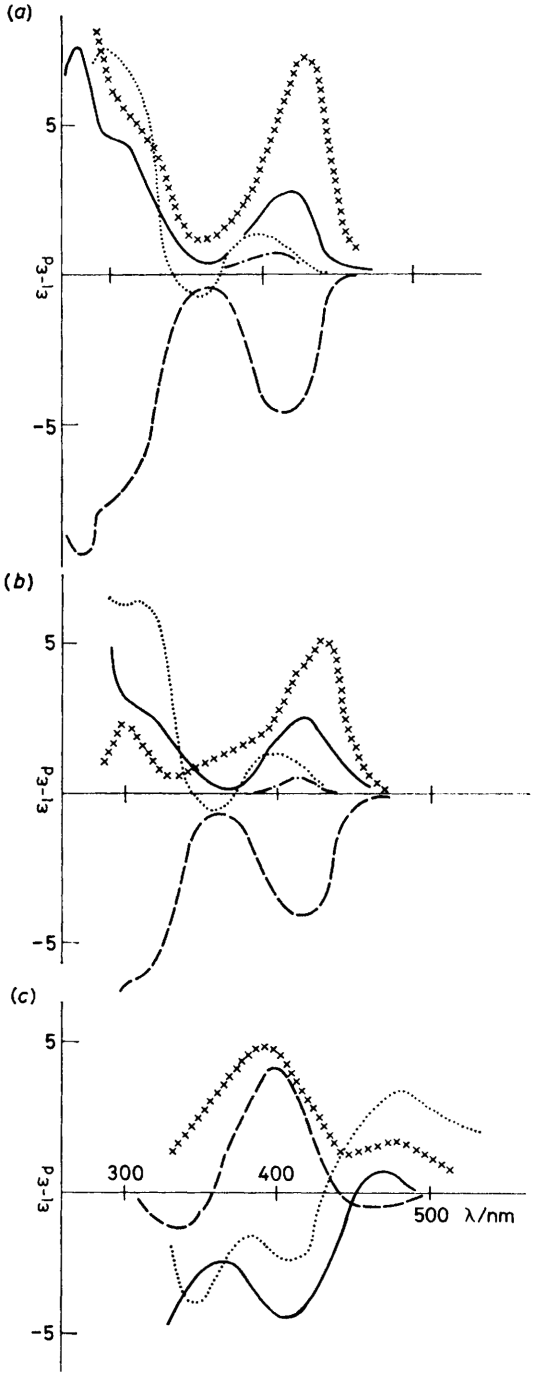


FIGURE 3 Circular dichroism spectra, in dmf solution (*a*), in chloroform solution (*b*), and in the solid state (*c*, KBr pellets, arbitrary units) of [PdL]. Symbols for the diamines are as in Figure 2

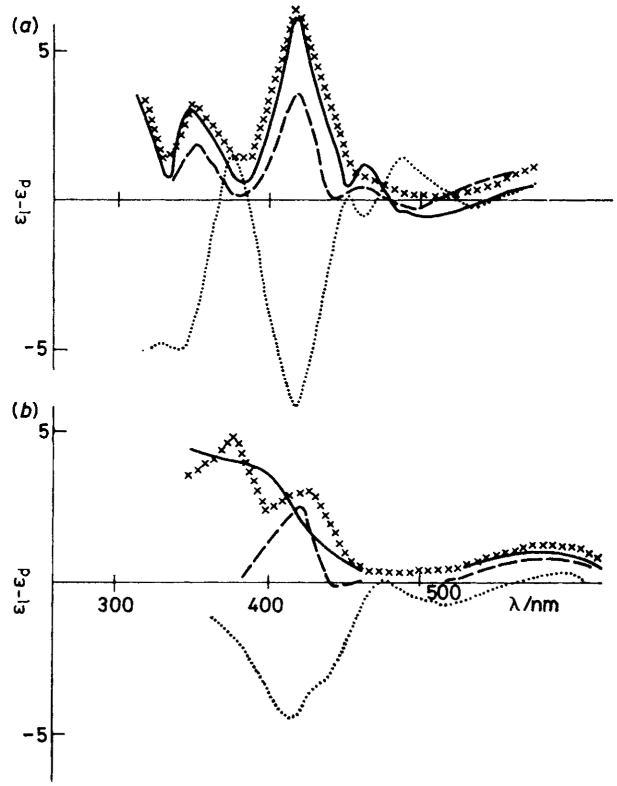


FIGURE 4 Circular dichroism spectra in chloroform solution (*a*) and in the solid state (*b*, KBr pellets, arbitrary units) of [NiL]. Symbols for the diamines are as in Figure 2

The spectra in dmf display the expected pattern for square-planar complexes with this type of quadridentate ligand. The conformations of the diamine chelate rings of the (—)pn, (—)bn, (—)pen, and (+)dpen complexes (axial substituents) are opposite to that of the (—)chxn complex (equatorial substituents), despite the fact that all the diamines have the same configuration (*R*). Opposite conformations give rise to nearly opposite patterns of the c.d. spectra.[3,6]

The spectra in chloroform have less clear general trends, particularly for [Pt{sal (+)dpen}] suggesting that the strong solvation of $CHCl_3$ affects the conformation of the quadridentate ligand, as would be expected. The ^1H n.m.r. spectra recorded in chloroform and dmf or dmso (Table 2; in the latter two polar solvents the n.m.r. and c.d. spectra are similar) are in agreement with this suggestion. The azomethine protons H^a (see Figure 1) resonate at δ 8.5 (relative to $SiMe_4$) in the polar solvents, with a coupling constant with ^{195}Pt of 76 Hz, whereas in $CDCl_3$ the signal is generally obscured by the complex absorption of the phenyl protons; only a small peak at *ca.* δ 8 can be observed, with an intensity consistent with the lower-field satellite due to the coupling of the two H^a protons with ^{195}Pt. This solvent effect on the chemical shift of the proton H^a may be due to a ligand conformation in $CDCl_3$, such that the azomethine hydrogen atoms interact at long range with some shielding region, probably that of the phenyl rings. In dmf, however, the proton H^a is likely to be planar with the phenyl–azomethine system, thus being in the expected deshielding region. This conformational change is confirmed by the solvent effect on the coupling constant

J(Pt–H) of the protons of the diamine chelate ring (H^b) which is dependent on the dihedral angle, θ, Pt–N–C–H^b [13] (Figure 1). For example, the coupling constant ^1H-^{195}Pt varies from 36 Hz in dmf to 18 Hz in $CDCl_3$ for the (+)dpen complex. This large difference reflects a change in conformation of the diamine chelate ring between the two solvents. From the values of the coupling constant and of the chemical shift of H^a, we conclude that the ligand is almost planar in dmf, with the diamine chelate ring normally *gauche* [2] [H^b equatorial, R and R′ axial; see Figure 1(*b*)], whereas in chloroform the strong interaction with solvent molecules distorts the ligand, with a lowering of the dihedral angle Pt–N–C–H^b [lower values of J(Pt–H^b)],[13] corresponding to a distortion of the ring towards an eclipsed conformation [see Figure 1(*d*)]. Complete inversion to a *gauche* (H^b axial, R and R′ equatorial) conformation is not likely since it should completely reverse the signs of the bands of the c.d. spectrum.[6]

The strong solvation with $CHCl_3$ has not been observed in the case of [Pt{sal(−)bn}]; with this complex, the value of 42 Hz for the coupling constant $^1H^b$–^{195}Pt in $CDCl_3$ corresponds to a large value of θ as expected for the conformation reported in Figure 1(*b*) (H^b equatorial, R = R′ = CH_3 axial).[13] In addition, the chemical shift of the azomethine hydrogen atoms and their coupling constant with ^{195}Pt are rather similar in both $CHCl_3$ and dmf solution (Table 2) suggesting a similar geometry of the ligand in both solvents, in agreement with the very similar c.d. spectra in the two solvents. The behaviour of [Pt{sal(−)bn}] confirms the greater stability of the diaxial conformation for this particular ligand since it is sterically very difficult to accommodate two methyl groups in a pseudo-diequatorial eclipsed arrangement as required by strong $CHCl_3$ solvation.[14]

TABLE 2

Hydrogen-1 n.m.r. spectral data [a]

Compound	Solvent	Benzene ring	H^a	H^b	Other protons
[Pt(salen)]	dmf	6.4—7.6 (m)	8.57 (s) [J(H–Pt) = 76]	3.91 (s) [J(H–Pt) = 32]	
	dmso	6.3—7.6 (m)	8.45 (s) [J(H–Pt) = 76]	3.75 (s) [J(H–Pt) = 33]	
[Pt{sal(−)pn}]	$CDCl_3$	6.2—7.5 (m)	8.1 [b] (s)	3.2—4.1 (m)	1.32 (d, J = 6.5)
	dmso	6.5—7.6 (m)	8.53 (s) [J(H–Pt) = 77]	3.5—4.2 (m)	1.38 (d, J = 6.5)
[Pt{sal(−)bn}]	$CDCl_3$	6.5—7.8 (m)	8.08 (s) [J(H–Pt) = 72]	3.46 (m) [c]	1.44 (d, J = 7)
	dmf	6.2—7.4 (m)	8.55 (s) [J(H–Pt) = 76]	3.65 (m) [c]	1.28 (d, J = 7)
[Pt{sal(*m*)bn}]	$CDCl_3$	6.5—7.6 (m)	7.67, 8.06 [d] (s)	4.1 (br), 3.4 (m)	1.33 (d, J = 7) 1.63 (d, J = 7)
	dmso	6.4—7.4 (m)	8.35, 8.46 [e] (s)	3.6, 4.0 (m)	1.27 (d, J = 6.5)
[Pt{sal(+)dpen}]	$CDCl_3$	6.1—7.3 (m)	7.43 [b] (s)	5.14 (s) [J(H–Pt) = 18]	7.2 (s)
	dmf	6.3—7.8 (m)	8.45 (s) [J(H–Pt) = 76]	5.33 (s) J(H–Pt) = 36]	7.4 (s)
[Pt{sal(−)pen}]	dmso	6.1—7.3 (m)	8.50 (s) [J(H–Pt) = 75]	*ca.* 5 (m)	7.4 (s)
[Pd{sal(−)pn}]	$CDCl_3$	6.2—7.4 (m)	n.o.	3.1—4.3 (m)	1.28 (d, J = 6.5)
	dmf	6.4—7.5 (m)	8.05 (s)	3.2—4.2 (m)	1.37 (d, J = 6.6)
[Pd{sal(−)bn}]	$CDCl_3$	6.4—7.6 (m)	6.76 (s)	3.49 (q, J = 6)	1.41 (d, J = 6)
	dmf	6.5—8 (m)	8.34 (s)	3.85 (q, J = 7)	1.41 (d, J = 7)
	dmso	6.4—7.6 (m)	8.17 (s)	3.72 (q, J = 7)	1.32 (d, J = 7)
[Pd{sal(+)dpen}]	dmf	6.4—7.8 (m)	8.15 (s)	5.47 (s)	7.4 (s)
	dmso	6.4—7.8 (m)	8.20 (s)	5.36 (s)	7.4 (s)
[Pd{sal(−)pen}]	dmso	6.4—7.8 (m)	8.20 (s)	5 (m)	7.4 (s)
[Ni{sal(−)pn}]	$CDCl_3$	6.2—7.3 (m)	n.o.	2.7—4.0 (m)	1.38 (d, J = 6)
	dmso	6.4—7.5 (m)	7.96 (s)	2.9—3.8 (m)	1.36 (d, J = 6)
[Ni{sal(−)bn}]	$CDCl_3$	6.3—7.4 (m)	7.50 (s)	3.02 (q, J = 6.5)	1.47 (d, J = 6.5)
	dmso	6.4—7.4 (m)	7.97 (s)	3.5 (q, J = 6.5)	1.37 (d, J = 6.5)
[Ni{sal(+)dpen}]	$CDCl_3$	6.3—8.2 (m)	n.o.	4.49 (s)	7.4
	dmso	6.5—8.4 (m)	n.o.	4.79 (s)	7.4

[a] Values of δ in p.p.m. from $SiMe_4$ as internal reference, J in Hz. q = Quartet; n.o. = not observed, since signals are obscured by the phenyl protons resonances. Due to low solubility, the $CDCl_3$ spectra of some compounds have not been recorded. [b] The integration of this signal is consistent with $\frac{1}{3}$ of a proton, presumably it is the lower-field satellite due to the coupling with ^{195}Pt, the resonance of the uncoupled azomethine proton being obscured by the signals of the benzene ring. [c] Quartet (J = 7 Hz) coupled with ^{195}Pt [J(H–Pt) = 42 Hz]. [d] Two singlets of intensity corresponding to one proton {both coupled with ^{195}Pt[J(H–Pt) = 72 Hz]}. [e] Two singlets of intensity corresponding to one proton {both coupled with ^{195}Pt[J(H–Pt) = 76 Hz]}.

Palladium Complexes.—From the values of the chemical shift of H^a (Table 2), the same chloroform solvation can be proposed for the related palladium(II) and nickel(II) complexes. However, strangely enough, the palladium(II) complexes show c.d. spectral patterns which are unusual for square-planar complexes of quadridentate Schiff bases of the type described here.[6] The c.d. spectra of [Pd{sal(−)chxn}] both in dmf and in chloroform (Figure 3) are not opposite to those of the other diamines with the same absolute configuration (Figure 3) as in the corresponding complexes of Pt^{II} (Figure 2) and Ni^{II} (Figure 4). Since the only possible conformation of the chelate ring of chiral cyclohexanediamine is that with the substituents diequatorial,[3,6] we must assume that the palladium derivatives have, in solution, the conformation with equatorial substituents, Figure 1(*c*). This is most unusual, since such a conformation is the most stable for five- and particularly six-co-ordinated complexes with this class of ligand but not, with the obvious exception of complexes of chiral chxn, for square-planar complexes.[6] Furthermore, it is not likely that five-co-ordination can be achieved by solvation of the palladium(II) ion, at least with $CHCl_3$, whilst six-co-ordination is not usual for palladium(II) compounds. In any case, the electronic spectra (which are similar for both dmf and $CHCl_3$ solutions) are not those expected for five-co-ordinate palladium(II) complexes.[15]

Weak five-co-ordination could be realised by dimerisation through interaction of the Pd atom with the phenolic oxygen atoms of another molecule {as for instance in the so-called inactive form of [Co(salen)][16]}. However, this hypothesis must be ruled out since the complexes have been found to be monomeric in $CHCl_3$ through accurate molecular-weight measurements (Table 2).

Therefore, it appears that quadridentate Schiff bases of the type H_2L display with Pd^{II} an unusual conformational behaviour in which the substituents at the carbon atoms of the diamine chelate ring are preferentially bis equatorial. The only exception is [Pd{sal(—)-bn}] as can be inferred from both c.d. (Figure 3) and n.m.r. spectra (Table 2), confirming once again the stability of the diaxial conformation of this ligand.

In addition, while platinum(II) and nickel(II) complexes show similar c.d. spectra in the solid state and in solution (see Figures 2 and 4), the solid-state c.d. spectra of the derivatives of Pd^{II} have rather complicated patterns quite unlike those obtained in solution (Figure 3).

Conclusions.—In a previous paper [6] we tried to define some general rules for the conformational behaviour of complexes with the quadridentate Schiff bases formed between salicylaldehyde and optically active 1,2-diamines and we correlated the conformation of the diamine chelate ring with the overall co-ordination number of the metal ion. In particular, the factors affecting the conformation of the four-co-ordinate square-planar complexes appeared to be well established. In the present work, however, we have found that while the planar platinum(II) complexes behave as expected, the derivatives of Pd^{II} do not follow the general rule. No straightforward reason can be put forward as to why the palladium compounds show the anomalies reported here, however, it is likely that these anomalies have a parallel in the profound difference in reactivity between Pt and Pd, such as the observed difference in the activity of these complexes as hydrogenation catalysts ($Pd \gg Pt$).[9]

In particular, it has been proposed that the catalytic properties of [Pd(salen)] could be attributed to a partial dissociation of the quadridentate ligand; [7] this would give rise to a conformationally more flexible species which could account for the observed anomalies of the c.d. spectra. Moreover, we have observed that the c.d. spectra do not change appreciably when recorded under a hydrogen atmosphere or in the presence of cyclohexene, showing that these reagents do not alter the conformation of these complexes.

It is also likely that the failure to achieve asymmetric hydrogenation of prochiral substrates using palladium(II) complexes of chiral Schiff bases as catalysts is related to the anomalies discussed above, since some reactions catalysed by complexes of these chiral Schiff bases with other metals have been reported to occur with reasonably high asymmetric yields.[5,17]

EXPERIMENTAL

Analyses were by the microanalytical laboratory of the University of Milan. Circular dichroism spectra were recorded on a Jobin Yvon mark III instrument; ^1H n.m.r. spectra were obtained with a Varian NV 14 (60 MHz), or with a Varian XL100 (100 MHz) instrument. Molecular weights were measured in chloroform with a Hewlett–Packard 302B osmometer.

Preparations of the Schiff bases [18] and of the nickel(II) complexes [6] have already been described. Literature methods were used to prepare $[Pd(OC_6H_4CHO)_2]$,[10] $[Pd(diamine)Cl_2]$,[19] $[Pt(diamine)Cl_2]$,[20] *cis*-$[Pt(NCMe)_2Cl_2]$,[21] and *cis*-$[Pd(NCPh)_2Cl_2]$.[22] The compounds $Tl_2[L]$ and $Tl[OC_6H_4CHO]$ were prepared by mixing an ethanol suspension of $Tl[OC_2H_5]$ with an ethanol solution of the appropriate Schiff base H_2L or salicylaldehyde.

Preparation of the Complexes.—*Route* (i).[7] Palladium sponge was treated, under nitrogen, with fuming nitric acid, heated to secure complete dissolution, and evaporated to dryness *in vacuo*. The cold residue was treated with an equimolar amount of the appropriate Schiff base dissolved in anhydrous ethanol. The yellow precipitate was filtered off, washed with ethanol, and crystallized from chloroform.

Route (ii). Freshly prepared $[Pd(OC_6H_4CHO)_2]$ [10] was suspended in a chloroform solution of an equimolar amount of the diamine and stirred for 2 h. The yellow compound was filtered off and crystallized as above.

Route (iii). Solid $Tl_2[L]$ was added to a solution of *cis*-$[Pt(NCMe)_2Cl_2]$ in CH_3CN or of *cis*-$[Pd(NCPh)_2Cl_2]$ in ethanol. The suspension was refluxed for 24 h and evaporated to dryness on a rotary evaporator. The solid was extracted on a Soxhlet apparatus with chloroform; the resulting solution was concentrated and treated with light petroleum (t.p. 60—90 °C) to give a yellow material which was filtered off and crystallized from chloroform.

Route (iv). The compounds $[M(diamine)Cl_2]$ and $Tl[OC_6H_4CHO]$ (mol ratio 1 : 2) were mixed in dmf or pyridine and heated at 60 °C for 3 days (M = Pt) or stirred at room temperature for 24 h (M = Pd). The white precipitate of TlCl was filtered off and the solution was evaporated to dryness with a rotary evaporator. The residue was extracted with chloroform, as above.

All four routes were used successfully for palladium [yields from 90%, route (i), to 60%, route (iv)], whereas the platinum complexes could be obtained only from routes (iii) (yields 50%) and (iv) (yields 60—70%).

[0/994 *Received*, 26*th June*, 1980]

REFERENCES

[1] Part 5, E. Cesarotti, M. Gullotti, A. Pasini, and R. Ugo, *J. Chem. Soc., Dalton Trans.*, 1977, 757.

[2] M. Calligaris, G. Nardin, and L. Randaccio, *Coord. Chem. Rev.*, 1972, **7**, 385.

[3] B. Bosnich, *J. Am. Chem. Soc.*, 1968, **90**, 627; R. S. Downing and F. L. Urbach, *ibid.*, 1968, **90**, 5344; 1969, **91**, 5977; 1970, **92**, 5861; R. L. Farmer and F. L. Urbach, *Inorg. Chem.*, 1970, **11**, 2562.

[4] M. Gullotti, L. Casella, A. Pasini, and R. Ugo, *J. Chem. Soc., Dalton Trans.*, 1977, 339.

[5] H. Aoi, M. Ishimori, S. Yoshikawa, and T. Tsuruta, *J. Organomet. Chem.*, 1975, **85**, 241; M. Ishimori, H. Aoi, T. Takichi, and T. Tsuruta, *Chem. Lett.*, 1976, 654.

[6] A. Pasini, M. Gullotti, and R. Ugo, *J. Chem. Soc., Dalton Trans.*, 1977, 346 and refs. therein.

[7] G. Henrici Olivé and S. Olivé, *Angew. Chem., Int. Ed. Engl.*, 1974, **13**, 549.

[8] W. Sawodny, M. Reiderer, and E. Urban, *Inorg. Chim. Acta*, 1978, **29**, 63; W. Sawodny and M. Reiderer, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 859.

[9] E. Cesarotti and R. Ugo, unpublished work; F. Cariati, M. L. Ganadu, F. Castelli, E. Cesarotti, and A. Pasini, XIth National Conference of Inorganic Chemistry, Cosenza, Italy, 1978. Società Chimica Italiana and Associazione Italiana Chimica Inorganica, Comm. 3A.

[10] L. Sacconi, M. Ciampolini, F. Maggio, and G. Del Re, *J. Am. Chem. Soc.*, 1960, **82**, 815.

[11] W. P. Schaefer and R. E. Marsh, *Acta Crystallogr., Sect. B*, 1969, **25**, 1675.

[12] E. N. Baker, D. Hall, and T. N. Waters, *J. Chem. Soc. A*, 1970, 406.

[13] S. Yano, T. Tukada, M. Saburi, and S. Yoshikawa, *Inorg. Chem.*, 1978, **17**, 2520.

[14] A. Pasini, M. Gullotti, L. Casella, and P. Romagnoli, *Inorg. Nucl. Chem. Lett.*, 1975, **11**, 705; M. Gullotti and A. Pasini, *Inorg. Chim. Acta*, 1975, **15**, 129.

[15] L. M. Venanzi, *Angew. Chem., Int. Ed. Engl.*, 1964, **3**, 453; C. Furlani, *Coord. Chem. Rev.*, 1968, **3**, 141.

[16] S. Bruckner, M. Calligaris, G. Nardin, and L. Randaccio, *Acta Crystallogr., Sect. B*, 1969, **25**, 1671.

[17] Y. Fujii, M. Sano, and Y. Nakano, *Bull. Chem. Soc. Jpn.*, 1977, **50**, 2609.

[18] M. Gullotti, A. Pasini, P. Fantucci, R. Ugo, and R. D. Gillard, *Gazz. Chim. Ital.*, 1972, **102**, 855.

[19] B. J. McCormic, E. N. Jaynes, jun., and R. I. Kaplan, in ' Inorganic Syntheses,' ed. F. A. Cotton, McGraw-Hill, New York, 1972, vol. 13, p. 216.

[20] G. L. Johnson, in ' Inorganic Syntheses,' ed. H. F. Holtzclaw, jun., McGraw-Hill, New York, 1966, vol. 8, p. 242.

[21] K. A. Hofman and G. Bugge, *Berichte*, 1907, **40**, 1776.

[22] M. S. Karasch, R. C. Sayler, and F. R. Mayo, *J. Am. Chem. Soc.*, 1938, **60**, 882.