Chiroptical Properties of Five-co-ordinated Olefin Complexes of Platinum(II)

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The chiroptical properties of five-co-ordinated complexes of general formula $[PtCl_2(N–N)(olefin)]$, with olefin ligands having either electron-donating or electron-withdrawing substituents, have been investigated. A comparison is also made with related square-planar complexes. The optical properties and the c.d. spectra of several enantiomers are reported. A correlation rule between the sign of the c.d. bands in the regions around 29 000 and 44 000 cm^{-1} and the absolute configuration is found for complexes containing prochiral ethylene homologues. For both bands a positive sign seems to be diagnostic for the *R* configuration.

The quadrant rule, proposed by Scott and his co-workers,[1] provides a general method for the assignment of the absolute configuration of chiral or prochiral olefin ligands† in square-planar Pt^{II} complexes.[2] In particular, it has been found that the sign of the lower-field c.d. band in the 23 000—27 000 cm^{-1} region, attributed to a *d–d* transition, is strictly related to the position of the substituent groups of the olefinic bond. This relationship is summarized in Figure 1.

The rule is applied to neutral,[3] anionic,[4] or cationic[5] Pt^{II} complexes. A comparison between Pt^{II} and Rh^{I} has been recently made by Saito[6] after examination of the c.d. spectra of chiral olefin complexes. While the spectrum in the 20 000—30 000 cm^{-1} region appears to depend on the metal, a strong band centred at *ca.* 40 000 cm^{-1}, attributed to a π–π^* transition of the alkene, seems to be correlated only with the configuration of this ligand.

A new class of trigonal bipyramidal complexes, of general formula $[PtCl_2(N–N)(olefin)]$, has been described.[7] The olefin ligand can be either an ethylene homologue or an alkene bearing an electron-withdrawing substituent. Very few and ill-characterized square-planar Pt^{II} complexes with the latter class of ligands are known.[8] This study reports an investigation of the chiroptical properties of trigonal bipyramidal complexes containing a variety of prochiral olefin ligands. The main aim of this work is to look for a correlation rule between absolute configuration and c.d. spectra of these complexes.

Results and Discussion

Synthesis of Chiral Complexes.—Essentially pure or partially resolved enantiomers of complexes of formula $[PtCl_2(N–N)(olefin)]$, where olefin = propene (**a**), but-1-ene (**b**), (*E*)-but-2-ene (**c**), (*E*)-hex-3-ene (**d**), (*E*)-cyclo-octene (**e**), acrolein (**f**), and acrylonitrile (**g**) and N–N = butane-2,3-dione bis-*NN*-dimethylhydrazone (**1**), 2-t-butylaminomethylenepyridine (**2**), and ethane-1,2-dione bis-*N*-t-butylimine (**3**), have been prepared and characterized. Enantiomers of complexes of (*E*)-but-2-enedinitrile (**h**) with (**1**) and (**2**) have been also prepared. Our attempts to synthesize (**3h**) were unsuccessful.‡

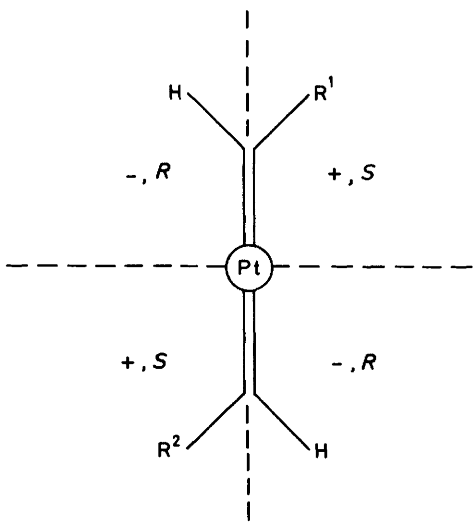

Figure 1. Quadrant rule for square-planar Pt^{II}–olefin complexes

The syntheses were made as outlined below. In the case of the olefins (**c**)—(**e**), the procedure involves a square-planar diastereoisomer as the starting material (RNH_2^* is (*R*)- or (*S*)-$[NH_2CH(CH_3)C_6H_5]$) (Scheme 1). The period of standing in solution for the complexes can be restricted to a few minutes. With the olefins (**c**) and (**d**) the racemization rate is slow enough that the final product is still obtained in substantial enantiomeric excess (see below). Of course, in the case of chiral (**e**) no racemization is involved in the reactions. When the olefin is propene (**a**) or but-1-ene (**b**) the above method is unsuitable owing to high racemization rates. Therefore a one-step procedure using an ionic diastereoisomer was utilized (Scheme 2) $\{RNMe_3^{*+}$ is (*S*)-$[(CH_3)_3NCH(CH_3)C_6H_5]^+\}$. The pro-

trans-$[PtCl_2(olefin)(RNH_2^*)] + HCl + PPh_4^+Cl^- \longrightarrow$
diastereoisomer
$PPh_4^+[PtCl_3(olefin)]^- + RNH_3^{*+}Cl^-$
enantiomer

$PPh_4^+[PtCl_3(olefin)]^- + N–N \longrightarrow$
enantiomer
$[PtCl_2(N–N)(olefin)] + PPh_4^+Cl^-$
enantiomer

Scheme 1.

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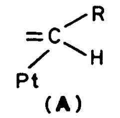
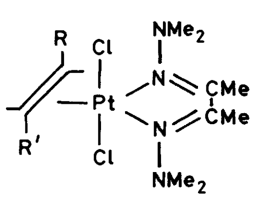
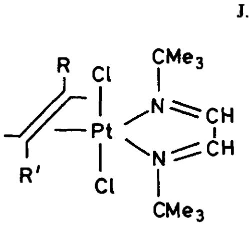
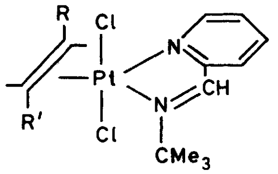
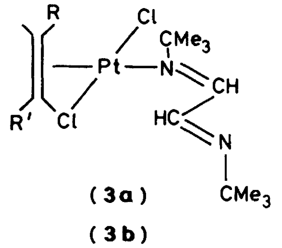
† The notation 'configuration of the olefin' will be used to indicate the configuration of the chiral carbon in (**A**).



(**A**)

‡ We note that we are unable to obtain racemic (**3h**) by olefin exchange starting from $[PtCl_2(ethylene)(N–N)]$ [with N–N = (**3**)] and (**h**) in excess. After 24 h in benzene solution only a 5% exchange was observed by ^1H n.m.r. measurements.

R = H, R' = Me	(1a)	(2a)		(3a)
R = H, R' = Et	(1b)	(2b)		(3b)
R = R' = Me	(1c)	(2c)		(3c)
R = R' = Et	(1d)	(2d)		(3d)
R R' = $>(CH_2)_6$	(1e)	(2e)		(3e)
R = H, R' = CHO	(1f)	(2f)	(3f)	
R = H, R' = CN	(1g)	(2g)	(3g)	
R = R' = CN	(1h)	(2h)		

ducts have an enantiomeric excess and are suitable [except in the case of (**2a** and **2b**)] for the c.d. measurements notwithstanding the low optical purity of the starting material.[4b] The chemical purity of the complexes of (**a**)—(**e**) was checked by comparison of the ^{1}H n.m.r. data with those already reported[7] for the racemic complexes. All the compounds containing the N–N ligands (**1**) and (**2**) are five-co-ordinate, while the ligand (**3**) is monodentate and *trans* to the olefin.

$$\underset{\text{diastereoisomer}}{[RNMe_3]^{*+}[PtCl_3(olefin)]^-} + N\text{–}N \longrightarrow \underset{\text{enantiomer}}{[PtCl_2(N\text{–}N)(olefin)]} + RNMe_3^{*+}Cl^-$$

Scheme 2.

For the ligands (**f**)—(**h**), no stable square-planar Pt^{II} complexes are known which could be used as parent diastereoisomer in the preparation of a five-co-ordinated enantiomer.† Thus the stable[9] five-co-ordinated species [PtCl$_2$(Diam*)(olefin)]{where Diam* = (R,R)-[C$_6$H$_5$CH(CH$_3$)[N(CH$_3$)CH$_2$]$_2$} were used as the starting diastereomeric materials (Scheme 3). The products can be recrystallized without loss of optical purity. The analytical data confirm the reported formula. The ^{1}H n.m.r. parameters are listed in Table 1. All the complexes can be considered to be five-co-ordinate since the chemical shifts of the olefinic protons are comparable with those[9] of the starting five-co-ordinated complexes. We note that with the monosubstituted olefins (**f**) and (**g**) the restricted rotation of the unsaturated ligand around the Pt–olefin axis causes the non-equivalence of the two halves of the symmetrical ligands (**1**) and (**3**), as indicated by the doubling of the ^{1}H n.m.r. signals. In addition, in the case of the unsymmetrical ligand (**2**), this restricted rotation gives rise to two different geometrical isomers, which, at least in solution, are in nearly 1:1 and 3:1 ratios in the case of (**2f** and **2g**), respectively.

$$\underset{\text{diastereoisomer}}{[PtCl_2(Diam^*)(olefin)]} + 2HCl + N\text{–}N \longrightarrow \underset{\text{enantiomer}}{[PtCl_2(N\text{–}N)(olefin)]} + (DiamH_2^*)^{++} + 2Cl^-$$

Scheme 3.

Optical Activity of the Complexes.—The above synthetic methods allow a fairly large variety of complexes to be obtained whose dissymetry is due to preferential co-ordination of one face of the prochiral olefin ligand. Of course, in the case of complexes of (**e**) the olefin itself is chiral.

Table 2 reports the optical activities of the products. In the case of olefins (**a**)—(**d**), an estimation of the optical purity of the corresponding complexes can be made by comparing their optical rotations with those measured for the (E)-cyclo-octene compounds.[10] Taking into account that the sample of (−)-(E)-cyclo-octene is *ca.* 80% optically pure, a molar activity of 800° is attributed to each =CPtHCH$_2$– group in (**1e**). We assume that all =CPtHR groups have the same value in the pure enantiomers of the five-co-ordinated complexes (**1a**—**d**). We note that a molar rotation of 135° is reported[10] for =CPtHR in square-planar [PtCl$_2$(olefin)(RNH$_2$*)] complexes (both *cis*- and *trans*-stereoisomers). On the basis of previous observations, a nearly 100% optical purity can be assigned to (**1c**), (**1d**), (**3c**), and (**3d**), while only a 15—20% enantiomeric excess can be inferred for (**1a**), (**1b**), (**3a**), and (**3b**). This is consistent with the high optical purity and low racemization rate of the co-ordinated olefin both in the starting and the final compounds in case of olefin (**c**) and (**d**). In contrast, the optical purity of the starting material is low ($\leqslant$30%) in the case of the olefins (**a**) and (**b**) and a fast racemization of the co-ordinated olefin is also observed.

The optical purity of the complexes (**2a**—**d**), evaluated as above, seems generally lower than that obtained for ligands (**1**)

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† A simple method for obtaining the racemic complexes involves olefin exchange starting from the corresponding ethylene complex, in benzene solution or without solvent, if the olefin is a liquid.

Table 1. ^{1}H N.m.r. data of the [$PtCl_2$(N–N)(olefin)] complexes[a]

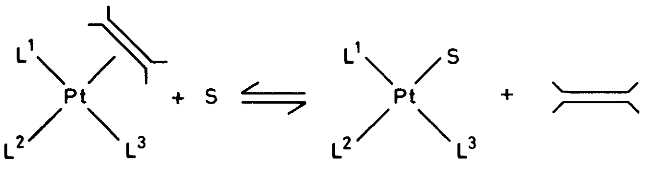
	Olefin		N–N ligand[b]			
Complex	Vinyl[c]	Others	C*H*=NR[d]	$(CH_3)_2NN=$	$(CH_3)C=NN$	$(CH_3)_3CN=$
(1f)[e]	4.28 (m), 4.17 (m), 3.72 (m)	9.79 (d)		3.08 (s), 2.99 (s)	2.52 (s), 2.49 (s)	
(2f)[f]	4.6 (m), 4.2 (m), 3.8 (m)	9.94 (d), 9.88 (d)	8.91 (s), 8.88 (s)			1.71 (s), 1.62 (s)
(3f)	4.45 (m), 4.15 (m), 3.75 (m)	9.80 (d)	8.76 (br s), 8.72 (br s)			1.69 (s), 1.61 (s)
(1g)[e]	3.75 (m), 3.67 (m), 3.47 (m)			3.11 (s), 3.00 (s)	2.55 (s), 2.52 (s)	
(2g)[g]	3.9 (m), 3.8 (m), 3.6 (m)		8.97 (s), 8.92 (s)			1.77 (s), 1.72 (s)
(3g)	3.86 (m), 3.73 (m), 3.50 (m)		8.81 (s), 8.76 (s)			1.72 (s), 1.66 (s)
(1h)[e]	4.05 (s)			3.05 (s)	2.61 (s)	
(2h)	4.31 (s)		9.01 (s)			1.76 (s)

[a] Spectra recorded at 270 MHz in $CDCl_3$ solution; chemical shifts are in δ with Me_4Si as internal standard. Legend: for multiplicity, s = singlet; d = doublet; m = multiplet; br = broad. [b] Average values of the chemical shifts of the pyridine ring protons in complexes (**2f**—**h**) are δ 9.2 (d), 8.1 (m), 7.9 (m), and 7.8 (m). [c] Coupling constants of the olefinic protons in all complexes are in the range 65—75 Hz. [d] Coupling constants of C*H*=NR protons in all complexes are in the range 40—50 Hz. [e] See ref. 11. [f] Mixture of two geometric isomers in *ca.* 1:1 ratio. [g] Mixture of two geometric isomers in *ca.* 3:1 ratio.

and (**3**). At least in part, this is due to the fact that crystallization of the more soluble complexes cannot be achieved quickly enough by comparison with the racemization time. The exceedingly low optical purity of complexes (**2a** and **b**) forbids c.d. measurements of these complexes.

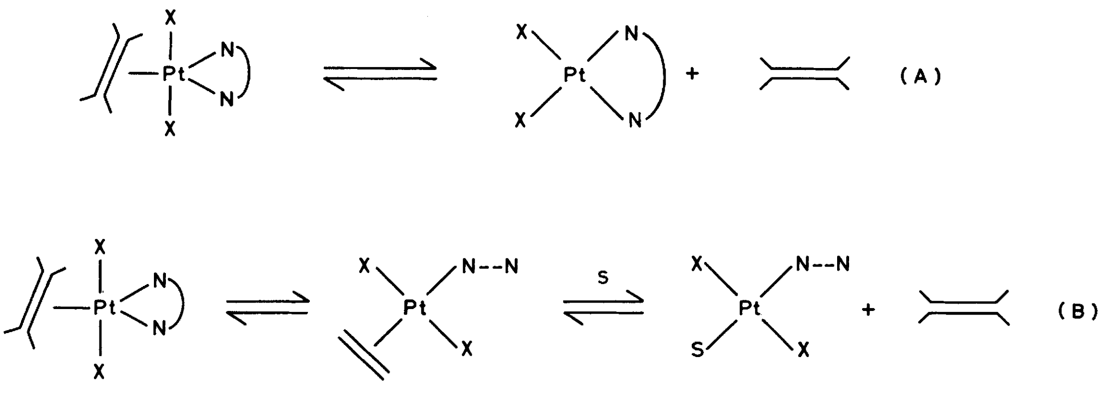
Nearly 100% optical purity is assigned to complexes containing electron-withdrawing olefins (**1h**) and (**2h**) by ^{1}H n.m.r. measurements, made in the presence of chiral shift reagents.[11] The shift reagent technique is unsuitable for complexes with monosubstituted olefins (**f**) and (**g**) because of overlapping of the multiplet signals of the olefinic protons. When N–N is (**2**) the presence of two geometrical isomers increases the difficulty of this approach.

Racemization Process.—Racemization in solution was observed for all complexes containing olefins (**a**—**d**). The rate of racemization depends on the solvent, the ligand N–N, and the co-ordinated olefin. At room temperature a half-time of a few hours was observed for complexes with the disubstituted olefins (**c**) and (**d**). The racemization half-times of complexes with the monosubstituted (**a**) and (**b**) are in the range of a few minutes (similar behaviour was observed[2b] for both neutral and anionic square-planar complexes). The complexes of (**1**) racemize more slowly than the corresponding complexes of (**2**) with the same olefin. However, additional data are required in order to rationalize the influence of N–N. A dramatic effect is found by comparing the racemization rates in chlorinated solvents and polar oxygenated solvents such as ethanol. When this latter solvent is used the rate is so high that no reliable measurements of the optical activity or the c.d. spectra of the propene or but-1-ene complexes could be made. The presence of free olefin in the solution causes a fast racemization. The racemization in the case of square-planar complexes is generally considered[12] to be a bimolecular process involving the solvent (Scheme 4).



Scheme 4.

Two types of mechanism are conceivable in the case of the five-co-ordinated complexes (Scheme 5). The solvent effect does not seem to fit mechanisms of type (A). Moreover, it has been found[13] that olefin release is not reversible, when X is a chloride ligand, at least when N–N is (**2**) or a similar ligand. Finally, the existence of an equilibrium in solution between the five-co-ordinated and the corresponding square-planar complex with a



Scheme 5.

Table 2. Optical activity data and c.d. spectral data for enantiomeric [$PtCl_2$(N–N)(olefin)] complexes

Complex	$[\alpha]_D$[a]	C.d. spectral data[b]						Solvent[c]	C*[d]
(1a)	−31	22 200 (−1.5)		27 900 (−6.5)	35 300 (+2.0)			$CHCl_3$	*S*
(2a)	>0								*S*
(3a)	+6		23 800 (+0.4)	30 100 (−1.8)	39 200 (+1.8)		41 600 (< −10)	$CHCl_3$	*S*
(1b)	−25	22 000 (−0.8)		28 500 (−5.0)	36 800 (+1.0)		41 600 (< −10)	$CHCl_3$	*S*
(2b)	>0								*S*
(3b)	+7		24 000 (+0.2)	29 500 (−0.5)	39 500 (+1.8)			$CHCl_3$	*S*
(1c)	−310	21 900 (−5.2)		27 200 (−23.8)	35 500 (+6.0)	38 500sh (+4.4)	45 000 (< −20)	EtOH	*S,S*
(2c)	+20	21 100 (−0.2)	23 800 (+1.8)	27 800 (−6.2)	35 600 (+6.0)	38 200sh (+4.2)	45 000 (< −30)	EtOH	*S,S*
(3c)	+59		24 800 (+5.4)	28 500 (−2.2)	33 800 (+2.0)	39 000sh (−8.0)	45 000 (< −30)	EtOH	*S,S*
(1d)	+250	22 000 (+2.8)		28 000 (+15.6)	36 400 (−3.8)	38 200sh (−2.7)	45 000 (> +20)	EtOH	*R,R*
(2d)	−52	21 700 (+0.1)	23 900 (−1.4)	28 000 (+4.0)	35 000 (−4.6)	38 000sh (−2.5)	45 000 (> +20)	EtOH	*R,R*
(3d)	−50		25 000 (−4.3)	29 800 (+3.5)		38 000sh (+5.3)	45 000 (> +20)	EtOH	*R,R*
(1e)	−220	21 900 (−7.5)		28 000 (−30.5)	35 800 (+20.0)	38 000sh (+15.0)	45 000 (< −30)	EtOH	*S,S*
(2e)	+45	20 800 (−0.4)	24 000 (+4.5)	28 000 (−9.0)	35 800 (+29.0)	40 800sh (+5.0)	45 000 (< −30)	EtOH	*S,S*
(3e)	+42		24 000 (+5.0)	28 700 (−8.0)	36 000 (+16.5)	40 000sh (+6.0)	45 000 (< −30)	EtOH	*S,S*
(1f)	−18	22 400 (−0.5)		28 300 (−3.4)	34 000 (>0)			$CHCl_3$	
(2f)	−60	22 200 (−0.5)		27 900 (−14.0)	36 000 (+16.0)	43 500 (−13.5)	45 000 (+10)	EtOH	
(3f)	−27	22 200 (−0.5)		28 000 (−8.0)		40 200 (+7.5)		EtOH	
(1g)	+2		24 400 (−1.5)	29 000 (+8.5)		42 000 (−12.0)		EtOH	
(2g)	<0		23 000 (+0.5)	29 600 (+6.0)	36 000 (−8.0)			EtOH	
(3g)	−27		22 800 (+0.4)	29 700 (+7.0)		41 600 (−12.0)		EtOH	
(1h)	−110		24 300 (+2.0)	28 600 (−13.0)		43 400 (+22.0)	47 000 (> +30)	EtOH	
(2h)	+72	22 200 (−0.7)	24 800 (+1.0)	29 400 (−13.4)	34 000 (> +20)			$CHCl_3$	

[a] For all complexes $c = 2.0$ in chloroform at 20 °C. [b] Significant maxima and shoulders (sh) in wavenumbers ($\times 10^{-3}$ in cm^{-1}) with $\Delta\Sigma$ (mol^{-1} dm^2) in parentheses. [c] Solvent used in c.d. measurements. [d] Absolute configuration of the chiral carbon in =C*PtHR.

monodentate N–N ligand *trans* to the olefin has been previously demonstrated[7] and proposed to be responsible of olefin exchange with retention of five-co-ordinate geometry.[14] Thus, the results are consistent with a mechanism of type (B).

Absolute Configuration of the Olefin and C.d. Spectra.—No question arises about the configuration (*i.e.* *S,S*) of the co-ordinated (**e**) in all its complexes since the olefin is chiral and does not epimerize in the conditions adopted.[15] The configuration of the prochiral olefins (**a**—**d**) in the complexes reported in this paper should be that of the starting square diastereoisomers (which is in turn given by the quadrant rule), since it is not expected that the synthetic procedures should involve inversion. Direct evidence of retention of configuration has been obtained by determining by *X*-ray analysis the absolute configuration (*S,S* in both cases) of the olefin in *trans*-[$PtCl_2${(*E*)-but-2-ene}(RNH_2*)] and in the five-co-ordinated complex (**1c**) derived from it.[16] In addition, no inversion is found[7] when the above diastereoisomer is allowed to react to give planar (**3c**). The olefin configuration, assigned according to the above considerations, for the complexes (**a**—**e**) is reported in Table 2.

When the c.d. spectra (see Figures 2 and 3 and Table 2) of the complexes (**1a**—**e**) and (**2a**—**e**), five-co-ordinated, and (**3a**—**e**), four-co-ordinated, are compared, some differences are observed which can be related to the co-ordination geometry. The general shape of the spectra appears to be related to the type of N–N ligand, as observed for the u.v.–visible spectra. In particular, the lower-energy region of the spectra shows the following features: (i) the sign of the optical bands at 24 000—25 000 cm^{-1} of the c.d. spectra of the square complexes (**3a**—**e**) is that anticipated by the quadrant rule; (ii) the spectra of the five-co-ordinated (**1a**—**e**) complexes show a band at 22 000 cm^{-1}; (iii) two bands of opposite sign are observed in the low-energy region of the spectra of the other five-co-ordinated complexes (**2a**—**e**), at *ca.* 22 000 (very weak) and *ca.* 24 000 cm^{-1}. When complexes of the

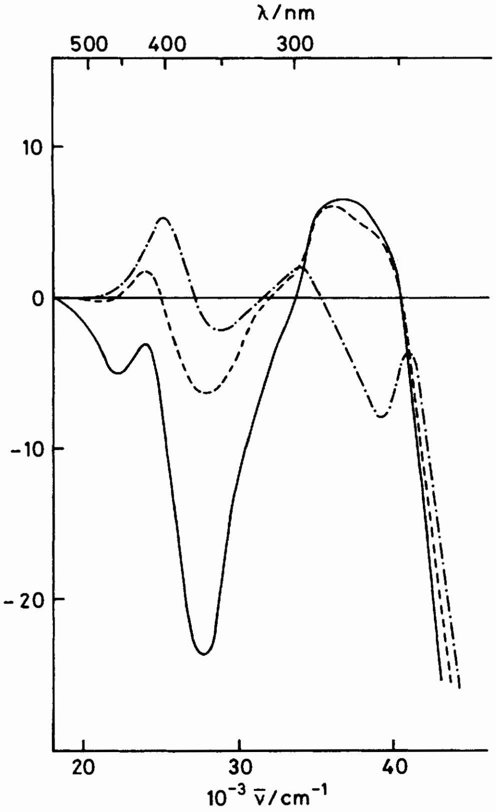


Figure 2. C.d. spectra, in ethanol solution, of Pt^{II} complexes with (*E*)-but-2-ene. Solid line, (**1c**); broken line, (**2c**); broken line with dots, (**3c**)

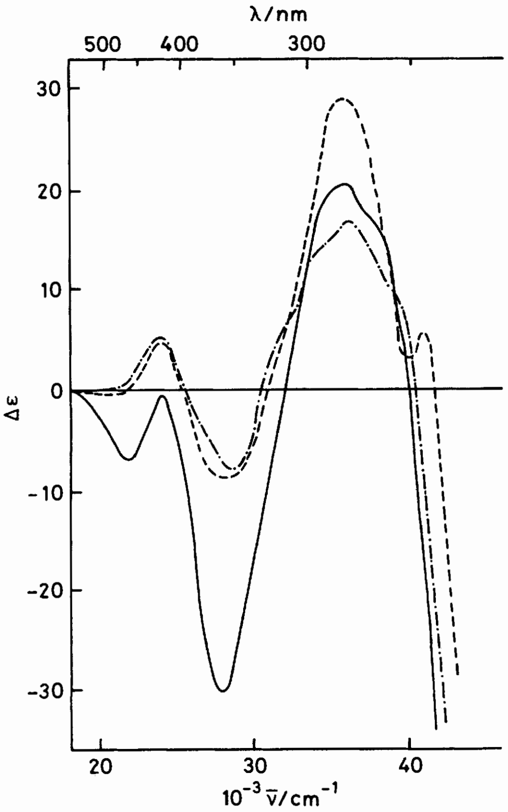


Figure 3. C.d. spectra, in ethanol solution, of Pt^{II} complexes with (*E*)-cyclo-octene. Solid line, (**1e**); broken line, (**2e**); broken line with dots, (**3e**)

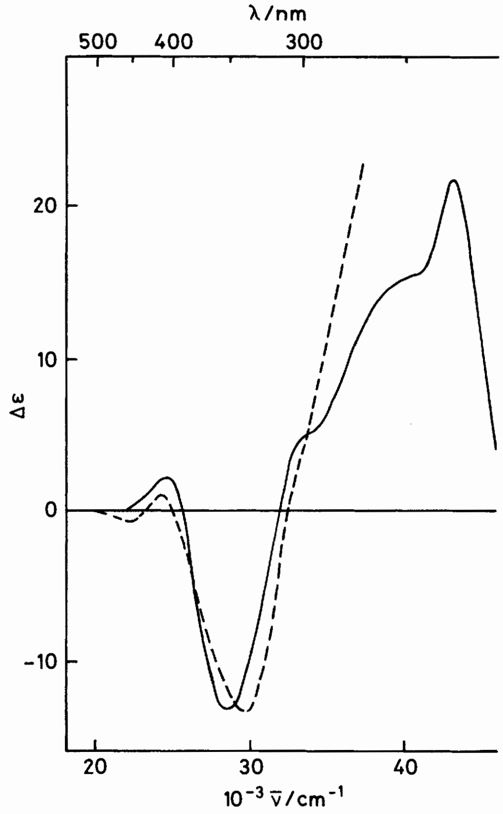


Figure 4. C.d. spectra of Pt^{II} complexes with (*E*)-but-2-enedinitrile. Solid line, (**1h**) in ethanol solution; broken line, (**2h**) in chloroform solution

same configuration are compared it is found that the former band coincides in sign with that exhibited by complexes of (**1**). On the other hand the sign of the 24 000 cm^{-1} band is the same as that shown by the spectra of the square complexes of (**3**) with the same configuration. In summary, the features of the spectra in the above discussed region do not appear to be the most suitable for a general correlation with absolute configuration.

Two regions of the spectra show a very similar shape for all complexes (**a**)—(**e**). An absorption maximum is always observed between 28 000 and 30 000 cm^{-1}. The sign of this band appears to be related to the configuration of the olefin ligand. More precisely, a positive sign seems to be diagnostic for the *R* configuration. In the region around 44 000 cm^{-1} a strong absorption is found, possibly due to a π–π^* transition for complexes with olefins (**c**)—(**e**). Since the c.d. spectra in this region must be determined in ethanol we could not perform the measurements for complexes (**1a**)—(**3a**) and (**1b**)—(**3b**) owing to fast racemization. Our data, on the whole, show that a positive band is associated with the *R* configuration.*

When the spectra of the complexes of olefins with electron-withdrawing groups are examined, it appears that the configuration of ligand (**g**) is opposite to that of (**f**) and (**h**). In fact, it is found that the sign of the band at *ca.* 29 000 cm^{-1} is positive for (**1h**) and (**2h**) (see Figure 4) and (**1f**)—(**3f**) while it is negative for (**1g**)—(**3g**). Up to now there is no basis for assuming that a positive band is diagnostic of the *R* configuration for this type of unsaturated ligand. Attempts to compare the high-

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* We note that the same correlations between c.d. bands and the olefin configuration can also be observed for the previously described[17] (+)-$[PtCl_2$(3-methylpent-1-ene)(butane-2,3-dione bis-*NN*-dimethylhydrazone)] complex.[18]

energy region absorptions for the two types of olefins are also complicated by the influence of transitions related to the CO and CN groups.

In summary, our results show that a clear correlation of the sign of at least one c.d. band with the absolute configuration does apply for five-co-ordinate Pt^{II}–olefin complexes, provided the species compared have substantially similar co-ordination environments. However, since several transitions contribute to the spectra, a more expanded correlation needs a detailed electronic assignment, and therefore a considerable increase in the experimental data.

Experimental

Solvents and reagents were of AnalaR grade. The N–N ligands were synthesized and stored under nitrogen. Platinum complexes were obtained and stored in air. ^1H N.m.r. spectra were recorded on a Bruker WH 270 MHz spectrometer; $CDCl_3$ was used as solvent and tetramethylsilane as internal reference. M.p.s were determined on a Kofler hot-stage apparatus. U.v.–visible spectra were obtained on a Perkin-Elmer 320 spectrophotometer in ethanol solution. Optical activities were determined on a Perkin-Elmer 141 polarimeter. The c.d. spectra were obtained on a JASCO J500-A spectropolarimeter. The elemental analyses were made in part by Analytische Laboratorien, Elbach, West Germany.

Starting Materials.—The N–N ligands (**1**),[19] (**2**),[13] and (**3**)[20] were synthesized and characterized as previously described. The starting diastereoisomeric olefin complexes were: (+)-[(*S*)-$RNMe_3$*]$^+$[$PtCl_3$(propene)]$^-$,[4b] $[\alpha]_D^{20}$ +1 [*c* 1.5, $(CH_3)_2CO$]. (+)-[(*S*)-$RNMe_3$*]$^+$[$PtCl_3$(but-1-ene)]$^-$,[4b] $[\alpha]_D^{20}$ +0.5 (*c* 1.5, $(CH_3)_2CO$). (+)-*trans*-{$PtCl_2$[(*E*)-but-2-ene][(*S*)-RNH_2*]},[20] $[\alpha]_D^{20}$ +46.1 (*c* 1.5, CH_2Cl_2). (−)-*trans*-{$PtCl_2$[(*E*)-hex-3-ene][(*S*)-RNH_2*]}. $[\alpha]_D^{20}$ −68.4 (*c* 2.0, CH_2Cl_2). This compound was obtained by adopting a procedure similar to that used for the (*E*)-but-2-ene complex.[21] The racemic mixture of *trans*-{$PtCl_2$[(*E*)-hex-3-ene][(*S*)-RNH_2*]} had $[\alpha]_D^{20}$ −11.1 (*c* 2.0, CH_2Cl_2). The (−)-diastereoisomer was crystallized from carbon tetrachloride as fine pale yellow needles, which change into an oil on losing solvent (Found: C, 35.4; H, 4.7; Cl, 15.25; N, 3.0. Calc. for $C_{14}H_{23}Cl_2NPt$: C, 35.7; H, 4.9; Cl, 15.1; N, 3.0%). (+)-*trans*-{$PtCl_2$[(*E*)-cyclo-octene][(*R*)-RNH_2*]},[15] $[\alpha]_D^{20}$ +58.8 (*c* 1.5, CH_2Cl_2).† (−)-{$PtCl_2$(acrolein)[(*R*,*R*)-Diam*]},[9] $[\alpha]_D^{20}$ −70 (*c* 1.5, $CHCl_3$). (+)-{$PtCl_2$(acrylonitrile)](*R*,*R*)-Diam*]},[9] $[\alpha]_D^{20}$ +89.0 (*c* 1.5, $CHCl_3$). (+)-{$PtCl_2$[(*E*)-but-2-enedinitrile][(*R*,*R*)-Diam*]},[9] $[\alpha]_D^{20}$ +43.0 (*c* 1.5, $CHCl_3$). PPh_4^+[$PtCl_3$(olefin)]$^-$ [olefin = (*E*)-but-2-ene, (*E*)-hex-3-ene, (*E*)-cyclo-octene]. All three diastereoisomeric compounds *trans*-[$PtCl_2$(olefin)(RNH_2*)] were transformed in the enantiomeric ionic PPh_4^+[$PtCl_3$(olefin)]$^-$ species. *trans*-[$PtCl_2$(olefin)(RNH_2*)] (5 mmol), dissolved in acetone, containing concentrated HCl (0.5 ml) at −10 °C was treated with an acid solution of aqueous PPh_4Cl (5.0 mmol). The solid precipitate, washed with cold water and dried, was characterized by standard procedures, without recrystallization, as the enantiomeric PPh_4^+[$PtCl_3$(olefin)]$^-$ species. PPh_4^+{$PtCl_3$[(*E*)-but-2-ene]}$^-$, $[\alpha]_D^{20}$ +56 (*c* 1.5, $CHCl_3$); PPh_4^+{$PtCl_3$[(*E*)-hex-3-ene]}$^-$, $[\alpha]_D^{20}$ −35 (*c* 1.5, $CHCl_3$); PPh_4^+{$PtCl_3$[(*E*)-cyclo-octene]}$^-$, $[\alpha]_D^{20}$ +32 (*c* 1.5, $CHCl_3$).

Synthesis of the Enantiomeric [$PtCl_2$(N–N)(olefin)] *Complexes.*—For the synthesis of the enantiomeric [$PtCl_2$(N–N)(olefin)] complexes three procedures were used depending on the olefin. The optical activities of the enantiomeric complexes are reported in Table 2. ^1H N.m.r. features for the complexes of the olefins (**f**)—(**h**) are reported in Table 1. The enantiomeric complexes of olefins (**a**)—(**e**) were characterized by ^1H n.m.r. spectroscopy, m.p.s, molecular weights, and elemental analyses which were identical with the physical data obtained for the racemic compounds.[7] All complexes with ligand (**1**) were obtained as orange-red crystals; the complexes of ligands (**2**) and (**3**) were yellow solids.

Olefin: propene (**a**) *and but*-1-*ene* (**b**). A thin powder of diastereoisomeric [(*S*)-$RNMe_3$*]$^+$[$PtCl_3$(olefin)]$^-$ (1.0 mmol) was treated with N–N (1.2 mmol) at −15 °C. The solid residue was washed with water, dissolved in acetone (0.5 ml), and quickly reprecipitated with water. The solids, obtained in good yield (>90%), were characterized as pure [$PtCl_2$(N–N)(olefin)].

Olefin: (E)-*but*-2-*ene* (**c**), (E)-*hex*-3-*ene* (**d**), *and* (E)-*cyclo-octene* (**e**). Enantiomeric PPh_4^+[$PtCl_3$(olefin)]$^-$ (1 mmol) dissolved in methanol (0.5 ml) was treated, on stirring, with N–N (1.1 mmol) at 0 °C. The solvent was evaporated until crystallization began. A first crop of [$PtCl_2$(olefin)(N–N)] was isolated and dried. After 2 h at −15 °C crystallization of the mother liquid was complete and the second crop of enantiomeric complex was isolated, washed with cold methanol, and dried (total yield 80%). The chemical purity of the two crops was substantially equal; the optical activity was slighty higher for the first.

Olefin: acrolein (**f**), *acrylonitrile* (**g**), *and* (E)-*but*-2-*enedinitrile* (**h**). Diastereomeric {$PtCl_2$(olefin)[(*R*,*R*)-Diam*]} (1 mmol) dissolved in acetone–methylene dichloride (2:1) (20 ml) was treated, on stirring, at 0 °C with 1M-HCl (2 mmol) and, after 5 s, with the N–N ligand (5 mmol). Adding water and evaporating the organic layer afforded an oil. Crystalline solids were obtained in 70—80% yields by dissolving the oils in methylene dichloride, drying on anhydrous Na_2SO_4, and recrystallizing by addition of ethanol.

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† From this material (−)-(*E*)-cyclo-octene was obtained with $[\alpha]_D^{20}$ −330 (*c* 2.0, hexane, corresponding to an optical purity of 80%.

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