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STERIC CONTROL IN THE STEREOSPECIFIC COMPLEXATION OF CHIRAL α-OLEFINS TO PLATINUM(II)

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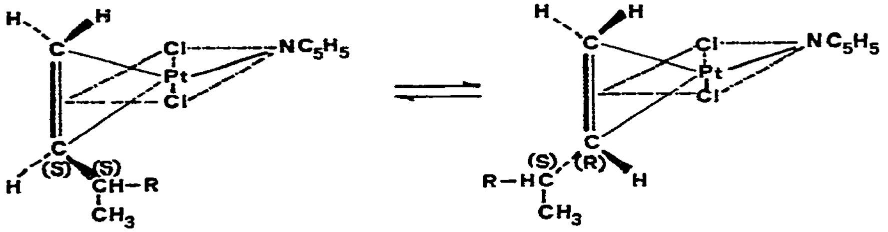
Summary

The complexes *trans*-dichloro[$R(CH_3)—C^*H—CH=CH_2$](pyridine)platinum(II), R = C_2H_5, i-C_3H_7, t-C_4H_9, have been prepared and their ^1H NMR and CD spectra investigated. The two diastereomers formed in the complexation of the chiral α-olefin to Pt^{II} are present in different concentrations in solution, the diastereomer of opposite absolute configuration at the two chiral centres being the prevailing one. The extent of stereoselectivity, evaluated both by NMR and CD, varies from 32% to 75% by changing the bulkiness of the R group. The preferred conformation of the two diastereomers for each complex has been established by NMR, taking into account the deshielding effect on the protons bound to saturated carbon atoms as well as J(H—H) and J(Pt—H) coupling constants.

Introduction

The study of olefin—platinum complexes affords an opportunity to speculate on the mechanism of the asymmetric induction observed in some important organic reactions such as hydroformylation, hydrogenation, and the polymerization of olefins. Indeed the reactive intermediates which are of value for the stereochemical pathway of the aforementioned reactions are inaccessible to direct or reliable observation and stable chiral olefin—platinum(II) complexes may be taken as useful models in their investigation [1].

Although the stereochemistry of a large variety of complexes of this type has been studied [1-3], very little is known yet on dichloro(olefin)(amine)platinum(II) complexes containing both a chiral α-olefin and an achiral amine.



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a) R = Et b) R = i-Pr c) R = t-Bu

Fig. 1. The pair of diastereomeric complexes.

In the formation of the above complexes a prochiral moiety, the olefin double bond, is converted into a chiral moiety, the linked double bond, under the intervening influence of a chiral centre (for instance an asymmetric carbon atom) present in the free olefin.

A pair of diastereomeric complexes are formed, using a chiral olefin with high enantiomeric purity, in dependence on which olefin "face" is bound to the transition metal (Fig. 1). The two diastereomers are convertible one into the other in solution by inversion of the chiral centre bound to Pt as a rapid ligand exchange occurs [4].

The extent to which one diastereomer is in excess over the other in the equilibrium condition is the percent stereoselectivity which is also, in this case, the percent asymmetric synthesis [5]. The stereoselective complexation of a chiral α-olefin to Pt^{II} has been shown in the case of *cis*- and *trans*-dichloro-$[C_2H_5(CH_3)\text{—}\overset{(S)}{C}H\text{—}(CH_2)_n\text{—}CH\text{=}CH_2](NH_2\text{—}CH_2\text{—}C_6H_5)Pt^{II}$ complexes [6] and the extent of stereoselectivity appears to be unaffected by the geometrical isomerism of the complex and to depend greatly on the distance between the two chiral centres in the complex.

In order to have a better insight into the influence of the olefin structure on the extent of stereoselectivity, we have investigated the series of complexes *trans*-dichloro-$[R(CH_3)\overset{*}{C}H\text{—}CH\text{=}CH_2].(C_5H_5N)Pt^{II}$ (Ia) ($R = C_2H_5$), (Ib) ($R = i\text{-}C_3H_7$), (Ic) ($R = t\text{-}C_4H_9$), in which two chiral centres are in the vicinal position and the olefin ligands have different steric hindrance levels.

Results

The preparation of the complexes I was achieved by displacing ethylene from the *trans*-dichloro(ethylene)(pyridine) platinum(II) complex by the suitable olefin.

The reaction was carried out in acetone using olefin samples containing at least 96% of the *S* antipode (optical purity ⩾ 92%) and quantitative yields of raw products were usually obtained.

The UV spectra of I (in chloroform) agree with those previously reported for Pt^{II} complexes of this type [7] and remain unchanged with time. Moreover, the samples of olefins recovered from the complexes I by displacement of the α-olefin with excess of ethylene [8] retained their original optical activity. All the complexes were recrystallized from a mixture of chlorinated and paraffinic solvents in order to obtain, by means of a second order asymmetric transformation [9], one of the two possible diastereomers in great prevalence. The diastereomeric composition of the crystallized samples was determined, as later shown, by NMR analysis.

The optical activity and circular dichroism, measured immediately after the dissolution of the samples, change with time because of the epimerization reaction which takes place in solution [1,6].

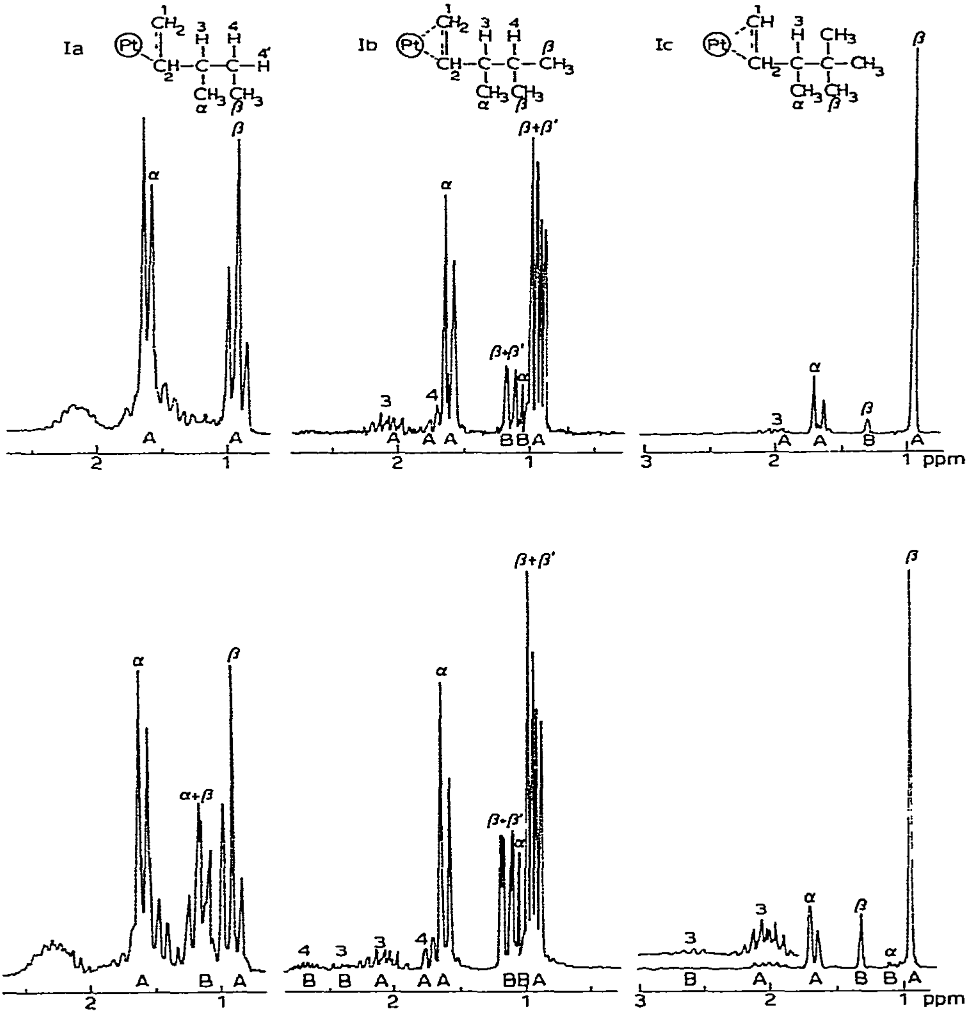


Fig. 2. ^{1}H NMR spectra of $CDCl_3$ solutions of the complexes I immediately after dissolution of the samples (upper) and after epimerization (lower).

NMR Spectra

The alkyl proton NMR resonances of complexes I performed immediately after dissolution of samples and after several hours are reported in Fig. 2 "upper" and "lower", respectively. In time all the spectra show the appearance or the growth of some signals at the expence of others and are interpretable on the basis of the presence in solution of two diastereomeric complexes A and B.

a. Chemical shifts. The complex Ia [10] shows a doublet at δ 1.58 and a triplet at δ 0.90 (Fig. 2 upper) assignable to the resonances of the $CH_3(\alpha)$ and $CH_3(\beta)$ protons in the major diastereomer A. Furthermore, a multiplet of the H(3) for the same diastereomer is observable at δ 2.18 ppm while the signals of the diastereotopic protons H(4) and H(4′) are partially overlapped by the $CH_3(\alpha)$ resonances.

After short time, additional signals appear between the above resonances (Fig. 2 lower) at δ 1.16 and 1.10 which are assignable to the $CH_3(\beta)$ and $CH_3(\alpha)$ protons of the minor diastereomer B. On the left of the "lower" spectrum a multiplet appears which arises from the H(3) proton of both diastereomers, while the resonances of the H(4) and H(4′) protons are overlapped by the $CH_3(\alpha)$ doublet of the major diastereomer A. As far as complex Ib is concerned, both the "upper" and "lower" spectra clearly show the presence of the two diastereomers. The latter are characterized by the $CH_3(\alpha)$ resonances at δ 1.61 in A and δ 1.02 in B and by the resonances of the two diastereotopic $CH_3(\beta)$ and $CH_3(\beta')$ protons which appear as pairs of doublets at δ 0.91—0.95 in A and at δ 1.13—1.15 in B.

The resonances of the H(3) and H(4) protons of the two diastereomers appear as four multiplets on the left of the spectrum. The assignments reported in Fig. 2 have been carried out by double resonance experiments.

The good separation of the signals in the spectra of Ic makes the assignment of the resonances of the two diastereomers very easy in this case. The major diastereomer A is characterized by the doublet of the $CH_3(\alpha)$ at δ 1.66 and by the singlet of the $CH_3(\beta)$ at δ 0.92. The corresponding signals of B are observable at δ 1.06 and 1.29 respectively. In this case also the resonances of the H(3) proton in both the diastereomers are well separated and they appear as multiplets centered at δ 2.03 for A and at δ 2.59 for B.

The chemical shifts of the alkyl protons of complexed (δ′) and non-complexed olefins (δ), as well as the differences $\Delta\delta(\delta' - \delta)$, are reported for the three complexes I in Table 1.

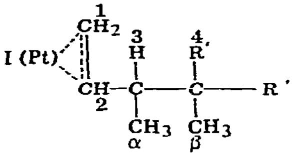
The Δδ of the $CH_3(\alpha)$ is higher for A than for B, while we note the opposite in the case of the $CH_3(\beta)$. Also, the H(3) and H(4) protons are deshielded in the complex, the Δδ being higher in the case of the diastereomer B. The very high Δδ value exhibited by the H(4) proton in diastereomer B of the complex I*b* should be noted.

b. Coupling constants. As far as the coupling constants are concerned, in Table 2 we give the vicinal coupling constants J[H(2)—H(3)], J[H(3)—H(4)] and the $J[Pt—CH_3(\alpha)]$ which are particularly interesting for stereochemical deductions.

However, while the platinum—$CH_3(\alpha)$ couplings are obtainable directly from the spectra, double resonance techniques were used to obtain the correct assignment and vicinal coupling constants for H(3) and H(4) protons.

TABLE 1

CHEMICAL SHIFT[a] OF THE ALKYL PROTONS OF THE OLEFIN NOT COMPLEXED (δ) AND COMPLEXED (δ') IN THE MAJOR A AND MINOR B DIASTEREOMERS (ppm FROM TMS) OF THE COMPLEXES I



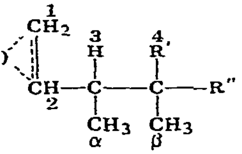
(Pt) = Pt—Cl_2—Py

Diastereomer	Complex	$CH_3(\alpha)$			$CH_3(\beta)$			H(3)			H(4)		
		δ'	δ	Δδ	δ	δ	Δδ	δ'	δ	Δδ	δ'	δ	Δδ
A (2*R*/3*S*)	Ia (R' = R'' = H)	1.58	0.96	0.62	0.90	0.85	0.05	2.18	2.02	0.16	n.d.	1.30	n.d.
	Ib (R' = H; R'' = CH_3)	1.61	0.94	0.67	0.91 0.95	0.84	0.07 0.11	2.10	1.94	0.16	1.65	1.48	0.17
	Ic (R' = R'' = CH_3)	1.66	0.93	0.73	0.92	0.84	0.08	2.03	1.90	0.13			
B (2*S*/3*S*)	Ia (R' = R'' = H)	1.10	0.96	0.14	1.16	0.85	0.31	2.36	2.02	0.34	n.d.	1.30	n.d.
	Ib (R' = H; R'' = CH_3)	1.02	0.94	0.08	1.13 1.15	0.84	0.29 0.31	2.39	1.94	0.45	2.70	1.48	1.22
	Ic (R' = R'' = CH_3)	1.06	0.93	0.13	1.29	0.84	0.45	2.59	1.90	0.69			

[a] In $CDCl_3$ at 20°C, δ' and δ correspond to complexed and non-complexed alkyl protons respectively, Δδ = (δ'—δ).

TABLE 2

SOME H—H AND Pt—H COUPLING CONSTANTS (Hz) IN THE MAJOR A AND MINOR B DIASTEREOMERS OF THE COMPLEXES I



(Pt) = Pt—Cl_2—Py

Diastereomer	Complex	J[H(2)—H(3)]	J[H(3)—H(4)]	J[Pt—$CH_3(\alpha)$]
A (2*R*/3*S*)	Ia R' = R'' = H	n.d.	≃7	2.7
	Ib R' = H; R'' = CH_3	10.5	≃1	2.7
	Ic R' = R'' = CH_3	13.1	—	2.7
B (2*S*/3*S*)	Ia R' = R'' = H	n.d.	n.d.	6.0
	Ib R' = H; R'' = CH_3	10.1	4.0	6.1
	Ic R' = R'' = CH_3	7.5	—	6.7

In the case of Ic, in particular, the irradiation at $CH_3(\alpha)$ signals of both A and B diastereomers gives two doublets from which the coupling constants J[H(2)—H(3)] were easily obtained. In the case of Ib the J[H(3)—H(4)] coupling constants of the minor diastereomer B were obtained by irradiation at $CH_3(\beta)$ protons. Successive irradiation at $CH_3(\alpha)$ protons gives a pair of doublets for H(3) from which the coupling J[H(2)—H(3)] was measured. For the A diastereomer it was not possible to operate in the same way owing to the overlapping of the H(4) and $CH_3(\alpha)$ signals. However, irradiation at the H(2) vinylic proton leaves only a quartet with a J coupling constant of 6 Hz for H(3) of A. The latter is easily assignable to $CH_3(\alpha)$—H(3) coupling and hence in this case J[H(3)—H(4)] has a very low value, of the order of the linewidth ($\simeq$1 Hz). Moreover, the unperturbed H(3) signal of A is easily interpretable on the basis of two coupling constants, i.e. the previously-obtained $J[CH_3(\alpha)$—H(3)] = 6 Hz and a J[H(2)—H(3)] = 10.5 Hz.

Attempts to determine the J[H(2)—H(3)] and J[H(3)—H(4)] coupling constants in the diastereomeric complexes Ia were unsuccessful with the sole exception of J[H(3)—H(4)] of A because of the complexity of signals.

Circular dichroism (CD) spectra

The CD spectra of I carried out at wavelengths between 350 and 500 nm in $CHCl_3$ show a negative band centred at about 400 nm (Fig. 3) which is assignable to the lowest energy *d*→*d* transition of *trans*-Pt^{II} complexes [11].

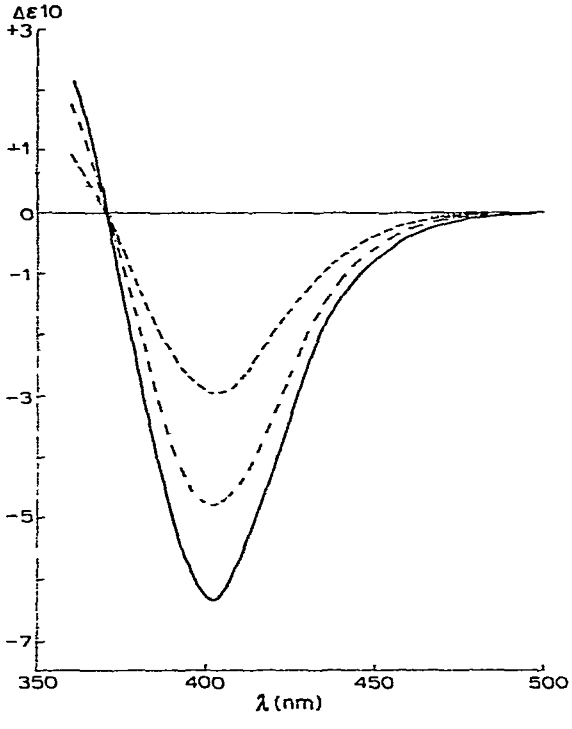


Fig. 3. Circular dichroism spectra in $CHCl_3$ of Ia (· · · · · ·), Ib (- - - - - -) and Ic (- · - · - ·) after epimerization and evaluated for the pure diastereomer A (2*R*/3*S*) of the same complexes Ia, Ib, Ic (———). All Δε values are corrected for the olefin optical purity.

TABLE 3

CD CHARACTERISTICS[a] AND DIASTEREOMERIC COMPOSITION OF THE *trans*-DICHLORO-$[R'{-}\underset{R''}{C}(CH_3){-}CH(CH_3){-}CH{=}CH_2](pyridine)Pt^{II}$ COMPLEXES

Complex		Absolute configuration of the olefin		$\Delta\epsilon^{\circ}$ [b]	$\Delta\epsilon^{\infty}$ [c]	$\Delta\epsilon^{*}$ [d]	Diastereomeric composition from NMR [f]			
		free	complexed				before epimerization		after epimerization	
							A%	B%	A%	B%
Ia	$R' = R'' = H$	*S*	*S*	−0.62	−0.20	−0.63	99	1	67	33
Ib	$R' = H; R'' = CH_3$	*S*	*S*	−0.46	−0.29	−0.64	86	14	75	25
Ic	$R' = R'' = CH_3$	*R*	*S* [e]	−0.58	−0.48	−0.64	95	5	87	13

[a] CD measurements carried out on chloroform solution at 20°C; all the data are corrected for the olefin optical purity. [b] $\Delta\epsilon_{max}$ at 402 nm measured immediately after dissolution of the sample. [c] $\Delta\epsilon_{max}$ at 402 nm after epimerization. [d] $\Delta\epsilon_{max}$ of a single diastereomer evaluated as $100 \times \Delta\epsilon^{\circ}/(\%A-\%B)$. [e] When the IUPAC system of nomenclature [18] is applied, the asymmetric carbon atom of the (*R*)-3,4,4-trimethylpentene formally assumes in the complex the *S* absolute configuration. [f] Determined from NMR spectra by integration of the alkyl protons resonances.

Whereas the wavelength of the above maximum does not change with time, the $\Delta\epsilon_{max}$ decreases in all cases reaching, after epimerization, a constant negative value ($\Delta\epsilon^{\infty}$) which is different for Ia, Ib and Ic (Table 3). The same values were reached faster in the presence of traces of free olefin. Also, the $\Delta\epsilon_{max}$ exhibited by the samples immediately after their dissolution in the solvent ($\Delta\epsilon^{0}$) are different for each complex.

On the contrary the $\Delta\epsilon_{max}$ of a pure diastereomer ($\Delta\epsilon^{*}$) evaluated by means the expression $\Delta\epsilon^{*} = 100 \times \Delta\epsilon^{\circ}/(\%A - \%B)$ [12] (Table 3) assumes a value quite close to −0.64 in all cases.

Discussion

Stereoselectivity

The diastereomerism originating from complexation of the chiral α-olefin to Pt^{II} is reflected in the room temperature ^{1}H NMR spectra of the complexes, especially in the region of the methyl-proton resonances which usually show well-separated signals; the concentration of diastereomers immediately after the dissolution of the samples and after epimerization can easily be determined by NMR spectroscopy.

As Fig. 2 "upper" shows, a diastereomer has been obtained in great prevalence by means of crystallization of the complexes Ia and Ic. For Ib a mixture of the two diastereomers (85/15) was obtained also after repeated crystallizations (Fig. 2 "upper").

In solution these complexes undergo an epimerization reaction until the equilibrium mixture shown in Fig. 2 "lower" is obtained.

The extent of stereoselectivity, defined as %A — %B [5], has been evaluated by determining the percent concentrations of the two diastereomers by NMR measurements on equilibrated solutions. As the asymmetric carbon atom α to

TABLE 4

EXTENT OF STEREOSELECTIVITY AND EQUILIBRIUM CONSTANT OF THE EPIMERIZATION REACTION FOR THE COMPLEX I

Complex	Stereoselectivity (%)		$K = [RS]/[SS]$ (at 20°C in $CHCl_3$)
	CD[a]	NMR[b]	
Ia	32	34	2.0 ± 0.1
Ib	46	50	2.8 ± 0.3
Ic	76	74	7 ± 1

[a] Determined by the relation $(\Delta\epsilon^{\infty}/\Delta\epsilon^{*})\cdot 100$. [b] Determined as (%A—%B) by the integration of the alkyl proton resonances.

the coordinated double bond does not influence the CD of the complexes [12] to a significant extent, the two diastereomers exhibit $\Delta\epsilon^*$ with the same absolute value and opposite sign; the percent of stereoselectivity can therefore easily be evaluated via CD by means of the expression $(\Delta\epsilon^{\infty}/\Delta\epsilon^*) \times 100$.

The values of stereoselectivity obtained by NMR and by CD measurements agree well (Table 4). The results obtained show that the complexation to Pt^{II} of chiral 3-methyl-substituted α-olefins occurs in a highly stereoselective manner, the extent of stereoselectivity being very large when R is the t-Bu group. Preliminary experiments carried out on Ia indicate that the nature of the solvent (benzene, acetone, chloroform) and the temperature (—30-+50°C) weakly affects the extent of stereoselectivity. Stereoselectivity decreases by a remarkable extent on increasing the distance between the asymmetric carbon atom and double bond [6]. The olefin structure thus seems to be the most important factor which influences the stereoselectivity in this type of complexes.

Configurational assignments

The configuration of the major diastereomer A for Ia was shown to be 2*R*/3*S* in the following manner. Crystallization of the complex is accompanied by second-order asymmetric transformation [9] and the solid material separated is composed of a single diastereomer as found for the analogous complex with the benzylamine. The latter has been shown by X-ray analysis to have a 2*R*/3*S* absolute configuration [10].

Interconversion of the diastereomers is observable in solution by NMR which shows that the diastereomer obtained by crystallization is also the most stable one. The sign of the CD band at 400 nm is negative both before and after epimerization. As also predicted by the sector rule, derived by Scott et al. [13], the negative sign of this band is related to the *R* absolute configuration of the chiral centre bound to Pt which to a great extent determines the CD observed. In the case of Ib and Ic, which also show negative 400 nm CD bands either before or after epimerization, it is quite reasonable to accept the validity of such a relationship and assign the 2*R*/3*S* configuration to the major diastereomer A and, of course, the 2*S*/3*S* configuration to the minor diastereomer B. According to the cases previously reported [6], the dominant diastereomer in solution in the equilibrium condition is characterized by different absolute configuration at the two chiral centres.

Conformational analysis

In order to rationalize the greater stability in solution of the $2R/3S$ diastereomer observed in all the cases examined, we have attempted to carry out conformational analysis of the olefin moiety in the diastereomeric complexes I.

The deshielding effect on protons bound to saturated carbon atoms, J(H—H) and J(Pt—H) as well as inspection of molecular models have been used for this purpose.

The downfield shift exhibited by alkyl protons in the complex with respect to the same signals in the free olefin has been inversely related to the platinum proton distance [10].

As the $\Delta\delta$ of the $CH_3(\alpha)$ protons is greater (Table 1) in the $2R/3S$ diastereomer (0.62—0.73 ppm) than in the $2S/3S$ one (0.08—0.14 ppm) in the former the $CH_3(\alpha)$ is nearer to the Pt atom. By contrast the $CH_3(\beta)$ protons show a larger $\Delta\delta$ (0.31—0.45 ppm) in the $2S/3S$ diastereomer and hence they are nearer to Pt in the latter case.

Further evidence for the greater proximity of the $CH_3(\alpha)$ to Pt in the $2R/3S$ diastereomer is provided by the $J[\mathrm{Pt—CH_3}(\alpha)]$ which was directly related to the Pt—$CH_3(\alpha)$ distance [14]. Indeed this coupling constant assumes the value 2—3 Hz in the $2R/3S$ diastereomers and 6—7 Hz in the $2S/3S$ ones.

The conformational arrangement around the C(2)—C(3) bond can also be deduced from the relative position of H(2) and H(3) protons, reflected in the J[H(2)—H(3)] coupling constant. Even if the latter is not easy to measure in Ia, as above reported, a quasi "*anti* position" of the two protons has been previously assumed for both diastereomers of this complex starting from X-ray analysis [10]. The above assumption can reasonably be extended to Ib which shows values of $CH_3(\alpha)$ and $CH_3(\beta)$ deshielding as well as of $J[\mathrm{Pt—CH_3}(\alpha)]$ close to the corresponding values of Ia (Tables 1,2). The high value of J[H(2)—H(3)] (10.1, 10.5 Hz) for the diastereomeric complexes Ib support the above hypothesis on the basis of a Karplus-type relationship [15].

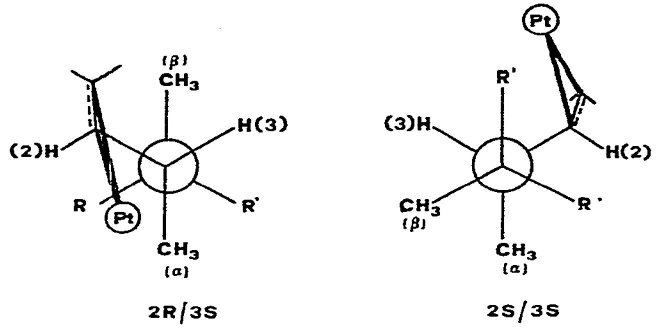
The difference between the J[H(2)—H(3)] values in the two diastereomeric complexes Ic suggests a less *transoid* position of H(2) and H(3) protons in the case of the $2S/3S$ diastereomer (7.5 Hz) compared with the $2R/3S$ one (13.1 Hz).

Taking into account the above results and inspection of molecular models, the pictures reported in Fig. 4 could be considered to be the limiting case of the preferred conformation of the diastereomeric complexes I. However some inconsistencies as far as the NMR data of the less stable $2S/3S$ diastereomers are concerned still have to be explained.

In order to have better insights into this problem we have carried out an approximate conformational analysis around the C(3)—C(4) bond. As previously reported [10], the relative positions of $CH_3(\alpha)$ and $CH_3(\beta)$ of Ia have been assumed to be *trans* and *gauche* in the $2R/3S$ and $2S/3S$ diastereomers, respectively.

Concerning Ib, the low values of J|H(3)—H(4)| in this case suggest a *cisoid* position of the H(3) and H(4) protons in both the diastereomers. At least in the case of the $2S/3S$ diastereomer, we may distinguish between the two possible *cisoid* positions as the H(4) proton bends towards the platinum, being much more deshielded than the H(3) proton (Table 1).

When there are no hydrogens on the C(4), as in Ic, owing to the strong



Ia $R' = R'' = H(4)$

Ib $R' = H(4)$; $R'' = CH_3$

Ic $R' = R'' = CH_3$

Fig. 4. Preferred conformation of the two diastereomeric complexes I. The Pt-Cl_2-Py moiety, (Pt), is bent towards the observer who is looking along C(3)—C(4) (2*R*/3*S*) or along C(4)—C(3) (2*S*/3*S*).

steric interaction between a methyl group and (Pt) (R′ and (Pt) Fig. 4), the t-butyl group moves from Pt by means of a rotation around the C(2)—C(3) bond. As a consequence the H(3) proton is nearer to Pt; this hypothesis is consistent with the higher deshielding effect on H(3) in the diastereomer 2*S*/3*S* of Ic than in the corresponding diastereomer of Ib. The preferred conformations of the complexed olefin in the two diastereomers point out that steric factors are of importance for producing stereoselectivity.

We may now attempt to analyze the stereoselective complexation in terms of the steric interactions which are stereochemically controlling. The position of the epimerization equilibrium and hence the steric diversity of the two olefin "faces" in the complex is mainly related to the difference between the steric interactions of the $CH_3(\alpha)$ or R group with the platinum moiety (Fig. 5).

The interaction $CH_3(\alpha)$---(Pt) determines differences in the thermodynamic stabilities of the 2*R*/3*S* diastereomers in the complexes I which are lower than those determined by the R---(Pt) interaction in the 2*S*/3*S* diastereomers. In other words, the main steric interaction has approximatively the same size in all 2*R*/3*S* diastereomers while it increases by increasing the bulkiness of the R group in 2*S*/3*S* diastereomers.

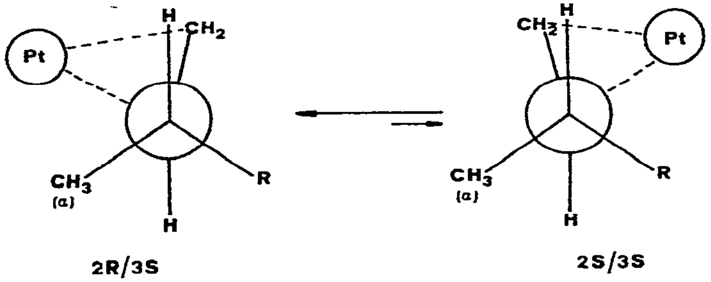


Fig. 5. Newman-type projection of the two diastereomeric complexes I along C(3)—C(2).

Therefore the difference between the thermodynamic stability of the two diastereomers of each complex I and hence the extent of stereoselectivity decreases in the order Ic > Ib > Ia.

As a final remark it is worth noting that the structure of the olefin may have an important role in determining the sign and extent of the asymmetric induction in reactions catalyzed by soluble transition metal complexes, when the coordination of the olefin to the catalyst is an important step for the stereochemical pattern of the reaction.

Experimental

Olefins

(+)(*S*)-3-methylpentene (b.p. 54°C, n_D^{25} 1.3842, $[\alpha]_D^{25}$ + 35.2°, optical purity 94%) was prepared by pyrolysis of the (+)(*S*)-3-methylpentylacetate [16] and purified by fractionation over metallic sodium.

(+)(*S*)-3,4-dimethylpentene (b.p. 81°C, n_D^{20} 1.3969, $[\alpha]_D^{25}$ + 41.0°, optical purity 94%) [8] and (+)(*R*)-3,4,4-trimethylpentene (b.p. 104°C, n_D^{25} 1.4100, $[\alpha]_D^{25}$ + 37.1, optical purity 92%) [17] were obtained resolving the corresponding racemic mixture by stereoselective complexation to the *cis*-dichloro[(*S*)-α-methylbenzylamine](ethylene) Pt^{II} complex, following the procedure previously reported [8].

Complexes

All the complexes were prepared by displacing ethylene from the *trans*-dichloro (ethylene)(pyridine)Pt^{II} complex in chloroform solution with the appropriate chiral olefin. Crude products collected as microcrystalline solids were dissolved in chloroform and recrystallized in the presence of traces of the corresponding chiral olefin by addition of n-pentane.

trans-dichloro[(+)(*S*)-3-methylpentene](pyridine)Pt^{II} (Ia): m.p. 111—113°C [10].

trans-dichloro[(+)(*S*)-3,4-dimethylpentene](pyridine)Pt^{II} (Ib): m.p. 116—118°C. Found C, 32.46; H, 4.29. $C_{12}H_{19}Cl_2NPt$ calcd.: C, 32.50; H, 4.32%.

trans-dichloro[(+)(*R*)-3,4,4-trimethylpentene](pyridine)Pt^{II} (Ic): m.p. 136—138°C. Found C, 34.01; H, 4.60. $C_{13}H_{21}Cl_2NPt$ calcd.: C, 34.13; H, 4.63%.

The chiral olefins were recovered from the respective complexes dissolving the latter in diethyl ether and pressuring the solution with ethylene. The complex *trans*-dichloro(ethylene)(pyridine)Pt^{II} is sparingly soluble and the chiral olefins were recovered by removal of the solvent after filtration of the solution.

Spectroscopic measurements

The spectra have been recorded at room temperature on $CHCl_3$ or $CDCl_3$ quickly-prepared solutions and on the same solutions after epimerization. UV spectra have been obtained by a Cary 14 spectrophotometer, CD spectra have been recorded by a Roussel-Jouan model II dichrograph and ^1H NMR spectra ($CDCl_3$ with TMS as internal standard) have been measured on a Jeol PS 100 spectrometer.

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