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TRIGONAL BIPYRAMIDAL PLATINUM COMPLEXES AS MODELS FOR ZIEGLER–NATTA CATALYTIC SITES

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Summary

Five-coordinated η^2-adducts of (+)-(S)-3-methyl-1-pentene (SMP) and (R,S)-3-methyl-1-pentene (RSMP) of the type [PtCl$_2$(η^2-olefin)(α-di-hydrazone)] were prepared. In solution the more stable adducts are those which have the olefin presenting to Pt the face of opposite configuration to that of the chiral substituent. In the solid state the same situation is found by X-ray analysis for the adduct of SMP, while ^{1}H NMR studies point to the conclusion that the same configuration as the chiral substituent is preferred in the solid adduct of RSMP. These observations are compared with those in previous reports on coordination of SMP on square planar Pt and stereoselective polymerization.

Introduction

Pino and his coworkers have described *trans* complexes of square planar Pt with chiral olefins, of general formula PtCl$_2$L(olefin) (where L = benzylamine or pyridine) and observed diastereoselective coordination of the olefin [1]. For example, coordination of the diastereotopic face of (+)-(S)-3-methyl-1-pentene (SMP) with absolute configuration [2] opposite to that of the sec-butyl substituent gave a more stable complex in solution than the other possible diastereomer. Paiaro and coworkers [3] had previously achieved enantioselective coordination of propylene on *cis*-PtCl$_2$L(olefin) complexes by using chiral L ligands. Bearing in mind that the isotactic specific polymerization of chiral olefins is stereoselective [4] and that Ziegler–Natta polymerization might involve coordination of the olefin to the metal atom of the active site before the insertion step [5], it is attractive to relate the observed enantioselective and diastereoselective coordinations on Pt^{II} to the enantioselective and diastereoselective incorporation of chiral α-olefins which ensures isotactic stereoselective polymerization as defined by Natta and coworkers [4,6,7].

However, it has recently been observed that in the isotactic polymerization of SMP, the more reactive face toward overall olefin incorporation is that having the same absolute configuration as the asymmetric sec-butyl substituent [8]. This conclu-

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sion was based on the analysis of the stereochemical structure of a suitably [8] enriched end group of poly-SMP by means of ^{13}C NMR spectroscopy and by assuming that the overall stereochemical mechanism of addition to the double bond is *cis* [9].

At present the implications of the observed dissimilarity between diastereoselective coordination on square planar Pt and diastereoselective insertion are uncertain. A systematic investigation of diastereoselective coordination on organometallic complexes could possibly afford some additional information on the structure of the active sites and on the mechanism of isotactic polymerization. As a first effort in this direction we report a structural study of the trigonal bipyramidal complex [$PtCl_2$(SMP)-{2,3-butanedione-bis(*N,N*-dimethylhydrazone)}] (SMP-Pt). The choice of this complex was dictated, among other reasons, by the fact that, unlike the more usually studied square planar complexes, it bears axial substituents, and thus might be a closer model to the active sites in the polymerization process [10].

Experimental

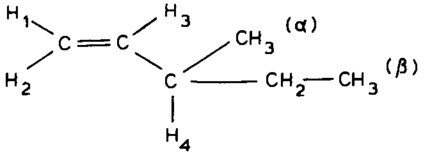
2,3-Butanedione-bis(*N,N*-dimethylhydrazone) [11] and (+)-(*S*)-3-methyl-1-pentene [12] were prepared by published methods. The syntheses and the ^1H NMR spectra of the complexes *trans*-[$PtCl_2$(SMP)(pyridine)] (SMPpy-Pt) [13] and *trans*-[$PtCl_2$(3-methyl-1-butene)(pyridine)] (MBpy-Pt) [14] have been previously described. Preparations and crystallizations of the complexes were carried out under nitrogen. Solvents were purified and distilled before use.

[$PtCl_2${(+)-(S)-3-methyl-1-pentene}{2,3-butanedione-bis(N,N-dimethylhydrazone)}] (SMP-Pt)

Liquid (+)-(*S*)-3-methyl-1-pentene (SMP) (2 ml) was added to 1.176 g (2 mmol) of finely-ground μ,μ'-dichloro-1,3-dichloro-2,4-bis(ethylene)diplatinum in a flask equipped with a dry ice condenser. The mixture was kept at the boiling point for about 15 min then the condenser was removed and the residual olefin evaporated. The ^1H NMR spectrum showed that the orange residue was nearly pure [Pt_2Cl_4{(+)-3-methyl-1-pentene}$_2$]. It was dissolved in the minimum amount of saturated aqueous solution of KCl and the solution was filtered. A solution of 0.680 g of the bishydrazone (4 mmol) in 5 ml of CH_3OH was added at 0°C and the precipitated orange oil was separated, washed with water, and dried. This crude oily product had $[\alpha]_D^{25}$ +66 (CH_2Cl_2, $c = 1.5$). Crystallization was achieved at −18°C from pentane, and gave deep orange crystals having $[\alpha]_D^{25}$ +202 (methylene chloride, $c = 1.0$). The optical activity of the solution slowly decreases with time (e.g. it falls to +177 after 20 min, at room temperature). The purity of the complex was confirmed by ^1H NMR spectroscopy (vide infra). The complex is stable in solution for several hours. Protic solvents enhance the decomposition.

The adducts of RSMP (RSMP-Pt) and of 3-methyl-1-butene (MB-Pt) were prepared similarly.

NMR measurements. Samples for NMR measurements were prepared by dissolving ca. 5 mg of the complex in 0.3 ml of the appropriate solvent contained in the NMR tube. Internal TMS was used as reference. All spectra were run with a probe temperature of 25°C on a Bruker WH-270 spectrometer using a 16K memory with 3K sweep width. Resolution enhancement was used in spectra employed for coupling constant measurements. Table 3 summarizes the chemical shifts of the olefin protons of the complexes SMP-Pt and RSMP-Pt. The shifts of the free olefin SMP and of the square planar complex SMPpy-Pt are also reported for comparison. The two sets of resonances labelled I and II refer to the two possible diastereoisomers.



X-Ray analysis of SMP-Pt

Crystal data: Monoclinic, $P2_1$, a 10.187(2), b 9.622(2), c 10.185(4) Å, β 98.43(3)°, $Z = 2$, $D_c = 1.75$, $D_{ob} = 1.73$. Radiation Mo-K_α, λ 0.7107 Å. The space group and the approximate cell unit dimensions were obtained from a preliminary photographic study; the final parameters were obtained by least squares refinement of 25 reflections.

Intensity data were collected on a CAD-4 Enraf Nonius automatic single crystal diffractometer in θ-ω mode up to $2\theta = 60°$. 3035 indipendent reflections were collected and corrected for polarization and Lorentz factors. 1830 reflections having $I < 3\sigma(I)$ were not considered in the refinement. The structure was solved by means of the Patterson method. The positions of Pt and Cl atoms thus derived yielded

TABLE 1

FINAL ATOMIC COORDINATES AND THERMAL PARAMETERS OF SMP-Pt[a]

Atom	x/a	y/b	z/c	B_{eq}[b]	B_{iso}
Pt	0.6797(1)	−0.34070(0)	0.3543(2)	4.38(5)	
Cl(1)	0.678(2)	−0.092(2)	0.355(1)	6.1(5)	
Cl(2)	0.684(1)	−0.574(1)	0.353(2)	5.7(7)	
N(1)	0.895(2)	−0.353(4)	0.322(2)		3.6(5)
N(2)	0.937(2)	−0.321(6)	0.194(2)		4.6(5)
N(3)	0.812(3)	−0.343(9)	0.552(3)		5.4(6)
N(4)	0.775(3)	−0.323(7)	0.678(3)		5.2(6)
C(1)	0.971(3)	−0.366(5)	0.428(3)		3.4(6)
C(2)	1.131(3)	−0.360(5)	0.410(3)		4.4(8)
C(3)	0.939(3)	−0.356(9)	0.554(3)		5.0(7)
C(4)	1.042(3)	−0.338(9)	0.670(4)		5.8(8)
C(5)	0.912(7)	−0.453(8)	0.132(7)		9.7(9)
C(6)	0.852(6)	−0.217(8)	0.099(6)		10.0(9)
C(7)	0.743(7)	−0.461(9)	0.694(7)		10.8(9)
C(8)	0.645(6)	−0.253(8)	0.654(7)		10.3(9)
C(9)	0.474(3)	−0.344(9)	0.348(3)		5.0(3)
C(10)	0.502(3)	−0.362(4)	0.221(3)		4.2(8)
C(11)	0.459(4)	−0.251(5)	0.120(4)		5.2(9)
C(12)	0.525(7)	−0.262(8)	0.009(7)		10.8(9)
C(13)	0.306(5)	−0.255(6)	0.083(5)		7.0(9)
C(14)	0.257(7)	−0.378(8)	0.023(7)		11.8(9)

[a] Estimated standard deviation in units of the last significant figure, are given in parentheses. [b] $B_{eq} = 4[(B_{11}B_{22}B_{33})/(a^{*2}b^{*2}c^{*2})]^{0.33333}$

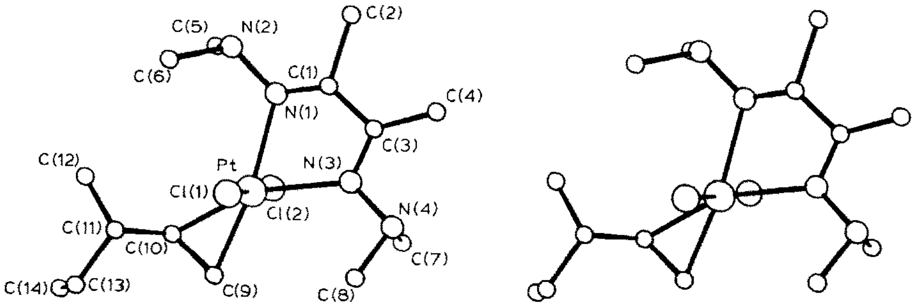


Fig. 1. Stereoscopic view of SMP-Pt as derived from the crystal structure analysis.

TABLE 2

RELEVANT MOLECULAR PARAMETERS [a]

Bond lengths (Å)		Bond angles (deg.)	
Pt–Cl(1)	2.39(2)	Cl(1)–Pt–Cl(2)	179.4(8)
Pt–Cl(2)	2.24(1)	Cl(1)–Pt–N(1)	93(1)
Pt–N(1)	2.25(3)	Cl(1)–Pt–N(3)	91(2)
Pt–N(3)	2.25(3)	Cl(1)–Pt–C(9)	90(3)
Pt–C(9)	2.08(3)	Cl(1)–Pt–C(10)	95(2)
Pt–C(10)	2.11(3)	C(9)–C(10)–C(11)	118(7)
C(9)–C(10)	1.37(4)	C(10)–C(11)–C(12)	112(7)
C(10)–C(11)	1.50(6)	C(10)–C(11)–C(13)	110(6)
C(11)–C(12)	1.40(7)	C(12)–C(11)–C(13)	113(7)
C(11)–C(13)	1.55(6)	C(11)–C(13)–C(14)	114(8)
C(13)–C(14)	1.40(9)		

[a] Estimated standard deviations in units of the last significant figure, are given in parentheses.

phase values good enough to locate most of the light atoms. The residual light atoms were identified by means of Fourier difference density maps.

Refinement was achieved by least squares procedures for all non-H atoms. Anisotropic thermal parameters were calculated only for Pt and Cl atoms. H atoms were introduced at stereochemically calculated position at the last stage of the refinement, with an isotropic thermal factor equal to those of the carrier atom. The final *R* value was 0.071.

A stereoscopic view of the molecule is shown in Fig. 1. All final positional parameters are reported in Tab. 1 and some relevant molecular parameter are reported in Tab. 2 *.

Results

Solution studies

The complexes SMP-Pt and RSMP-Pt were prepared and crystallized as described in the Experimental section. The crystals were dissolved in $CDCl_3$ and the ^1H NMR

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* A list of structure factors is availbable from the authors.

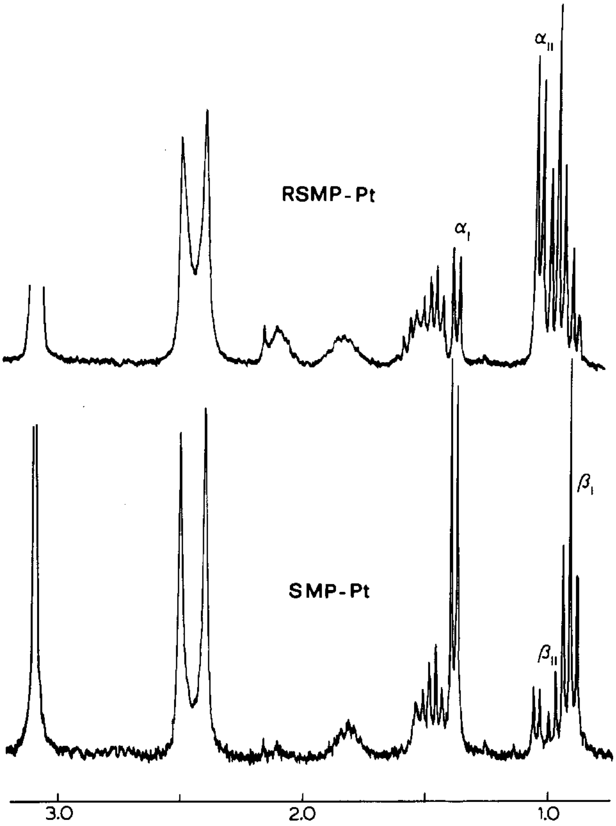

Fig. 2. High field portions of the 270 MHz NMR spectra of the trigonal bipyramidal complexes RSMP-Pt and SMP-Pt. The chemical shift scale is in ppm from TMS.

spectra recorded within 5 min. Figure 2 shows the 270 MHz spectra of both complexes. All the resonances can be readily assigned on the basis of comparisons with similar complexes [15] and by means of double resonance experiments; all the relevant assignments are reported in Tab. 3. It is important to note that the shapes of the N–CH_3 and C–CH_3 resonances of the dihydrazone (a sharp singlet at δ 3.088

TABLE 3

CHEMICAL SHIFTS OF THE PROTONS OF THE PARENT OLEFIN AND OF THE CORRESPONDING COMPLEXES [a]

	δ(1,2)	δ(3)	δ(4)	$\delta(CH_2)$	$\delta(\alpha CH_3)$	$\delta(\beta CH_3)$
SMP	4.88	5.64	1.97	1.258	0.923	0.807
SMP-Pt	3.57(I)	3.97(II)	1.84(II)	1.45(II)	1.047(II)	0.913(I)
	3.58(II)	4.08(I)	2.11(I)	1.56(I)	1.385(I)	0.973(II)
SMPpy-Pt	4.639(I)	5.33(I)	2.14(II)	1.381(I)	1.047(II)	0.849(I)
	4.641(II)	5.57(II)	2.29(I)	1.531(II)	1.531(I)	1.099(II)

[a] All chemical shifts are in ppm, referred to internal TMS. The shifts of the complex multiplets given by H(1), H(2), H(3), H(4) and CH_2 are only the centers of gravity of the resonances. The shifts of the two isomers of RSMP-Pt are not reported since they are identical to those of SMP-Pt.

TABLE 4

ISOMER PERCENTUAL COMPOSITION OF SAME PENTA- AND TETRACOORDINATED COMPLEXES OF SMP

Complex	Isomer	αCH_3	βCH_3
SMP-Pt	I	85	81
	II	15	19
RSMP-Pt[a]	I	26	25
	II	74	75
RSMP-Pt[b]	I	78	75
	II	22	25
SMP-py-Pt	I	67	66
	II	33	34

[a] Soon after dissolution. [b] After 15 h.

and a broad doublet at 2.457 ppm, respectively) reveal that the chemical exchange (caused by olefin rotation) is fast at room temperature. Thus the splitting of all the olefinic resonances can be attributed to the presence of the two possible diastereoisomers in comparable amounts. The clearly resolved resonances of the two methyl groups (the doublet labelled α and the triplet labelled β) allow a reliable estimate of the relative abundances. In the spectrum of SMP-Pt the resonances α_I and α_{II} account for 85 and 15% of the total methyl intensity, whereas the resonances labelled β_I and β_{II} account for 81 and 19%, respectively, of the β methyl intensity. Even at first glance it can be appreciated that the ratio between the populations of isomers I and II is reversed in the solution of RSMP-Pt (immediately after dissolution). Table 4 summarizes the relative intensities of the methyl resonances of the two isomers of SMP-Pt and RSMP-Pt. The corresponding values for the square planar complex SMPpy-Pt are reported for comparison. Ageing for ca. 15 h in $CDCl_3$ solution leads to a change in the isomer composition of RSMP-Pt, which ultimately approaches the equilibrium value for SMP-Pt. Equilibration is almost instantaneous in apolar solvents such as cyclohexane or benzene. The chemical shifts reported in Table 3 show that, besides the obvious changes in the resonances of the olefinic protons (H(1), H(2) and H(3)) complexation affects also the position of aliphatic resonances in a potentially diagnostic manner. All the changes are consistent with the spatial locations of the various groups, i.e. the resonances most affected by the complexation are those of groups facing the Pt atom, as can be seen in the molecular model based on the X-ray analysis (vide infra). Comparison with the chemical shifts of the square planar complexes [13,14] further suggests that the main isomer at equilibrium is the one with the methyl group facing the Pt atom and the ethyl group sticking out, a steric situation that corresponds to a configuration of the olefin face opposite to that of the sec-butyl substituent.

This finding is obviously based on complementary knowledge of the conformation around the $=C-CH(CH_3)C_2H_5$ bond. Complete analyses of the ABCX systems given by protons H(1), H(2), H(3) and H(4) were not attempted since most of the coupling constants involved were not of great relevance for our study: however it is rather easy to extract $J(H(3)H(4))$ coupling constants from these systems by means of a simple first-order analysis. Table 5 summarizes the values of these constants

TABLE 5

J(H(3)H(4)) COUPLING CONSTANTS (Hz)

Isomer	Complex				
	SMP-Pt	SMPpy-Pt	MB-Pt	MBpy-Pt	SMP
I	11.5_6	14.0_5	11.4_7	10	10.2_9
II	11.5_6	10.3_7			

together with those of square planar complex SMPpy-Pt of the corresponding penta-MB-Pt and tetra-coordinated MBpy-Pt complexes of methylbutene and of the parent olefin. In all cases the value is large enough to attribute a *trans* conformation to the C–H(3) and C–H(4) bands. In fact it has been pointed out long ago that the Karplus equation for such bonds is quite similar to that applying to two sp^3 carbons [16]. On the other hand it is not possible to attach a clear conformational meaning to the differences between the value for the free olefin and those for different complexes, since variations in electron densities may be sufficient to account for the differences.

Solid state studies

The crystal structure of SMP-Pt was determined by the Patterson method. The geometry of the coordination compound is trigonal bipyramidal. The chlorine atoms occupy the axial position, whereas the atoms C(9) and C(10) forming the double bond of SMP and the bidentate bishydrazone occupy the equatorial positions. Table 2 reports relevant molecular parameters. Bond lengths and angles are in good agreement with those for other Pt complexes [17,18]. Some discrepancies can be attributed to the quality of the diffraction data; good corrections for absorbtion were not feasible, owing to the shape of the tiny crystals used for data collection. However, the final R value obtained in the refinement (0.071) is satisfactory for the main objective of this crystal analysis, i.e. the determination of the relative configuration of asymmetric centers. As can be seen from Fig. 1, and in accordance with the NMR results, the configuration of the coordinated face of the olefin is opposite to that of the sec-butyl substituent, i.e. it is R.

Discussion and conclusions

Ziegler–Natta polymerization of α-olefins and catalytic hydrogenation are believed to share two fundamental reaction steps, i.e. coordination of the substrate to the metal atom of the catalytic complexes and migratory insertion. In fact the most generally accepted hypothesis on the reaction mechanism assumes that catalytic hydrogenation of olefins involves [19]: (i) formation of η^2-adduct between the substrate and the transition metal of the catalyst (Mt); (ii) oxidative addition of H_2 to Mt, and (iii), migratory insertion of the substrate on Mt–H and reductive elimination of the hydrogenated substrate. In the presence of asymmetric catalysts, asymmetric hydrogenation can be achieved [20]. Chan, Pluth and Halpern [21] were able to isolate the adduct [RhCl{(*S*,*S*)-chiraphos}(EAC)] *. Because of the asymmetry of chiraphos two diasteroisomeric adducts are possible, and the structure of the more stable diastereoisomer in solution does not correspond with the configuration of the *N*-acetyl-(*S*)-phenylanine ethyl ester obtained after hydrogenation, assuming H_2 addition on the face of EAC coordinated to the metal. Several possible explanations were offered, the most favoured being that the less thermodynamically stable adduct could be more reactive toward the subsequent hydrogenation.

As previously observed, adduct formation and migratory insertion via *cis* addition of Mt–R (where R = growing polymer chain) to the face of the olefin coordinated to the metal are believed to be fundamental steps also in Ziegler–Natta polymerization of α olefins [5–9]. When the olefin is chiral, diastereomeric monomer units may result from polymerization and the diastereoselectivity of the overall incorporation of the monomer was determined in previous papers [8] for SMP. We, like Lazzaroni and coworkers earlier [1], did not isolate any adduct of SMP with the active sites of the polymerization, but only determined the structure and the relative stabilities of diastereoisomeric coordination compounds of SMP which are supposed to mimic the stereochemistry of adduct formation in Ziegler–Natta catalysts. With this severe limitation in mind we may observe that coordination of SMP to both square planar and trigonal bipyramidal Pt is moderately diastereoselective, but the ratio between the concentrations of the diastereoisomers in solution is roughly reversed in comparison with that previously observed between the molar fractions of the diastereoisomer monomer units actually resulting from polymerization [8] *. In the five-coordinated complex of RSMP considered in this paper the relative concentrations of the diastereoisomers are reversed on going from the solid state to solution. This shows that the intermolecular forces in the crystal can be strong enough to reverse the driving force of the diastereospecific coordination. A similar situation could possibly occur on the surface of heterogeneous Ziegler–Natta catalysts, thus leading to the experimentally observed diastereoselectivity of the overall monomer incorporation [8].

Of course a different reactivity of the diastereoisomer adducts between SMP and Ziegler–Natta sites toward the subsequent insertion on Mt–R could equally well explain the reported results. At present there is too little information available to rule out other possible interpretations.

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* Here (*S*,*S*)-chiraphos = (2*S*,3*S*)-bis(diphenylphosphino)butane and EAC = ethyl-(*Z*)-α-acetamido cinnamate.

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