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Preliminary Communication

Conformational equilibrium in *trans,trans,trans*-cyclododecatriene (CDT). Studies on *trans*-dichloro(CDT)α-methylbenzylamine-platinum(II)

Gastone Paiaro and Paolo Ganis *

Dipartimento di Chimica Inorganica, Metallorganica e Analitica dell'Universita' di Padova, V. Marzolo 1, I-35131 Padova (Italy)

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Abstract

A pure diastereoisomer of the complex *trans*-[Pt(CDT)Cl_2{(*R*)-α-methylbenzylamine}] has been isolated. Circular dichroism and polarimetric measurements revealed the non-equivalence of the three diastereotopic olefin residues in the coordinated cycloolefin. This indicated a conformational equilibrium $D_3 \rightleftharpoons C_1$, which has been explained in terms of stereochemical and thermodynamic considerations.

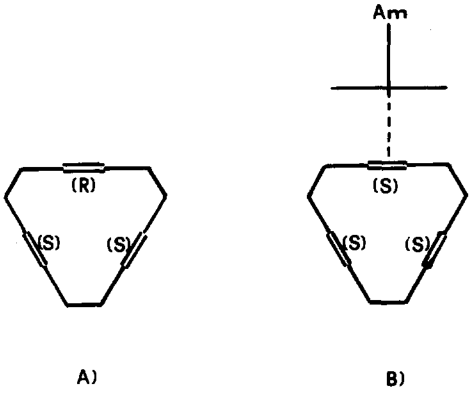
Key words: Circular dichroism; Polarimetry; Platinum; Olefin

Catalytic cyclooligomerization of 1,3-butadiene leads to an isomeric mixture of 1,5,9-cyclododecatrienes (CDT) [1]. The *trans,trans,trans* isomer, already characterized in the solid state by X-ray analysis [2], has received particular attention owing to its reactivity and its ability to form complexes with hetero-atoms located at the centre of the ring [3]. This isomer is an inherently dissymmetric molecule. It was resolved utilizing diastereoisomeric Pt^{II} complexes [4]. Besides the olefin moiety coordinated to Pt, the diastereoisomers of *trans*-[Pt(CDT)Cl_2{(*R*)-α-methylbenzylamine}] (**1a,b**) contain two free enantiotopic olefin residues. This prompted us to investigate more deeply the absolute configuration of CDT, to achieve stereospecific reactions at the unsaturated sites.

Only one diastereoisomer, **1a** [5] is formed on crystallization of **1a,b** from a solution of toluene–cyclohexane (1 : 1). This always occurs for Pt-olefin diastereoisomeric mixtures [6]. An almost pure sample of the positive diastereoisomer was obtained after successive crystallizations from toluene, up to the final $[\alpha]_D$ 209°. Figure 1 shows the corresponding CD spectrum. The bands at 402, 330, 302, 275 and 245 nm are assignable to the Pt-olefin complex [6]. The positive band at 402 nm indicates that the olefin group coordinated to Pt is in (*S*)-configuration, which corresponds to (*R*)-configuration in the free olefin. The positive band at 200 nm is attributable to the two uncoordinated *trans* double bonds. Comparison with the CD spectrum of (+)-(*S*)-*trans*-cyclooctene [7] enables us to assign an (*S*)-configuration to these olefin moieties, *i.e.* the opposite of that of the coordinated double bond.

The molecular rotation [M] of the pure diastereoisomer with the olefin bonded to Pt in the (*S*)-configuration is +1150°. The contributions to this value of the bound (+)-(*R*)-α-methylbenzylamine ($[M]_D$ +64°) as well as that of the coordinated olefin moiety (assumed to a first approximation to be equal to that of (*S*)-coordinated *trans*-2-butene ($[M]_D$ +270°) in the homologous Pt complex) are known [5]. Thus the value for each of the two free olefin moieties is estimated to be *ca.* +408° in the (*S*)-configuration, which is in fairly good agreement with that observed for free *trans*-cyclooctene in the same configuration ($[M]_D$ +450°) (neat), 414° (CH_2Cl_2) [7].

Therefore the CD and polarimetric data are unambiguously consistent with the absolute configuration shown below for uncomplexed (A) and complexed (B) CDT.



The question arises of what inhibits complexation with CDT units bearing all the three *trans* olefin groups in the same configuration.

The molecule of CDT in its ground state displays D_3 symmetry. Its molecular structure [2] has geometri-

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Correspondence to: Professor G. Paiaro.

* On sabbatical leave from the University of Napoli, Italy.

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cal parameters corresponding to almost theoretical values for a minimum internal energy; in particular, torsion angles about the =CH–CH_2– and the –CH_2–CH_2– bonds of 120° (*eclipsed* conformation) and 300° (*gauche* conformation) [8], respectively, (or 240° and 60° according to the chosen enantiomeric unit). It has been shown by iterative force-field calculations [9] that, starting from a D_3 molecular geometry, a rotation of 180° of one –CH_2–CH=CH–CH_2– residue about its two single sp^3–sp^2 bonds produces a C_1 conformation (*SRR* configuration) with an increase of internal energy of *ca.* 3 kcal/mol. Unless prohibitive molecular strains arise, such a rotation can occur randomly but on only one of the three olefin residues, so increasing the probability of CDT units in the C_1 conformation.

The ^{1}H-NMR spectrum (at 298 K) of the diastereoisomeric mixture (**1a,b**), when compared with that of the pure diastereoisomer **1a**, shows the expected two signals for the amine CH_3 protons and two signals for the vinyl protons of the coordinated olefin as the only differences. This proves either that in the starting Pt-complex CDT is solely in the *SRR* configuration or that the various isomers are indistinguishable by NMR spectroscopy. In both cases we cannot exclude the possibility that free or complexed CDT exhibits a conformational transition equilibrium of type (1).

$$\mathrm{CDT}(D_3) \rightleftharpoons \mathrm{CDT}(C_1) \qquad (1)$$

The relatively small increase of ΔH in C_1 is counterbalanced by a predictable increase of ΔS, which would probably favour this form. If so, in the reaction leading to the formation of the Pt-complex [4], the exchange with the form C_1 will be preferred and equilibrium (1) will be displaced to give a new C_1 form, to produce finally and quantitatively only the two diastereoisomers containing this form of CDT.

The pure diastereoisomer **1a** epimerizes in solution giving **1a,b** and attaining at equilibrium the molar rotation of the initial diastereoisomeric mixture. The epimerization reaction proceeds according to the rate law $k = \alpha/t$, where α is the degree of rotation. The measured $\Delta G^{\ddagger}$ in the range of 15–30°C is *ca.* 6 kcal, fully consistent with the reported data for a configurational ring inversion from a C_1 conformation [9]. This result supports our belief that in the Pt complex the *RRR* and *SSS* forms of CDT are absent.

Experimental details

The platinum complex was synthesized as previously reported [4,5]. The solvents employed were purified, dried and distilled before use. (+)-(*R*)-α-Methylbenzylamine was purchased from EGA Chemie and used without further purification.

The crude product was crystallized from a mixture of toluene-cyclohexane (1 : 1). In the course of three or four days at room temperature, successive fractions were obtained with an overall yield more than 80% of the original product with $[\alpha]_D$ 150°–170°. After subsequent recrystallizations from toluene, the pure product **1a** was isolated with a limiting value $[\alpha]_D$ 209°. *M.p.* 81°C; Analysis: found, C, 44.0; H, 5.0; N, 2.5; Cl, 12.8; Pt, 35.4; Calcd.: C, 43.8; H, 5.1; N, 2.6; Cl, 12.9; Pt, 35.6%.

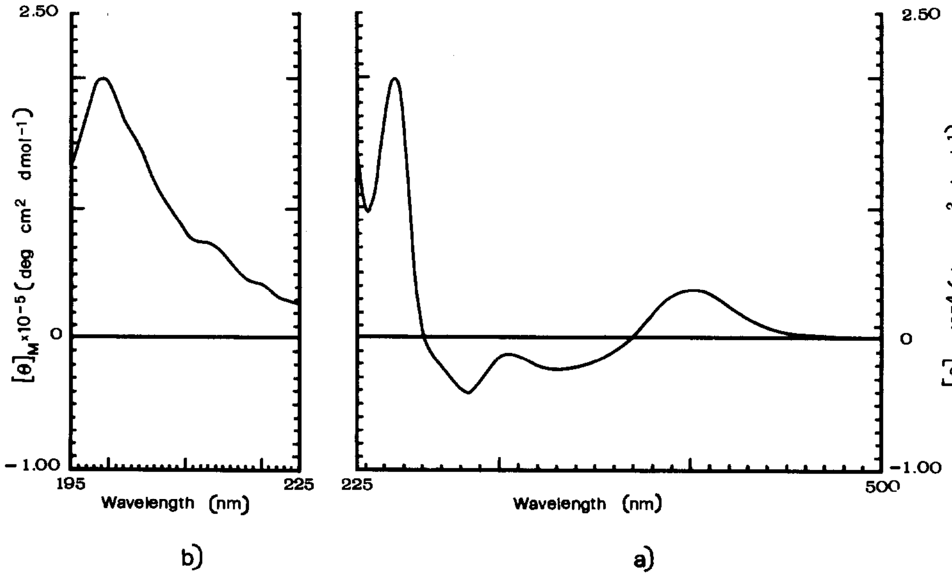

Fig. 1. (a) CD spectrum of **1a** in CH_2Cl_2 ($1.21 \cdot 10^{-3}$ M); (b) CD spectrum relative to the uncoordinated double bonds of **1a** in acetonitrile ($1.21 \cdot 10^{-3}$ M).

The pure diastereoisomer epimerizes in solution, attaining at equilibrium values of rotation corresponding to that of the initial diastereoisomeric mixture. This value expressed as molecular rotation [M] is almost the same as that of the ethylene complex [5].

Optical activities were measured on a Perkin Elmer 171 Polarimeter and CD spectra were recorded on a Jasco J-600 apparatus. ^{1}H-NMR spectra were recorded as CD_2Cl_2 solutions on a Bruker AC-200 spectrometer at 298 K. Elemental analyses were provided by the Microanalysis Laboratory of CIMA Department of the University of Padova.

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