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PLATINUM(II) AND PALLADIUM(II) COMPLEXES OF THIACYCLOOCT-4-ENES; AN UNUSUAL METAL-CATALYZED OLEFIN ISOMERIZATION

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Summary

Reactions of MCl_4^{2-} ($M = Pd, Pt$) with *cis*-thiacyclooct-4-ene, *cis*-2-methylthiacyclooct-4-ene and *cis*-2-phenylthiacyclooct-4-ene (*cis*-*S*-4-oct) give chelate complexes of general formula $MCl_2(cis-S-4-oct)$. X-ray structure determination indicates that coordination to the metal occurs through both the olefinic double bond and the sulfur atom. Reaction of CN^- with the adduct obtained from $PtCl_4^{2-}$ and a mixture of *cis*- and *trans*-2-methylthiacyclooct-4-ene liberates the *cis* ligand, and GLC analysis excludes the presence of free *trans* olefin. It is suggested that platinum complexes induce extensive *trans*→*cis* olefin isomerization.

Introduction

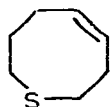
Much work has been carried out on complexes containing ligands bearing both an olefinic double bond and another donor atom; the work has mostly involved ligands containing a Group Va donor element. In particular platinum(II) chelate complexes of olefinic tertiary Group Va ligands have been widely studied [1–3], but only a few examples of palladium(II) and platinum(II) derivatives of ligands containing a Group VIa heavy donor atom and an olefinic double bond have been described; they were prepared from MX_4^{2-} ($M = Pd, Pt; X = Cl, Br$) and unsaturated sulfides or selenides of the type $RX(CH_2)_nCH=CH_2$ ($X = S, Se; n = 2, 3$) [4,5]. No examples of cyclic unsaturated sulfide metal complexes have been reported.

This study deals with the complexes of thiacyclooct-4-enes [6] ligands, in their *cis* and *trans* forms, with platinum(II) and palladium(II), together with evidence for an unusual platinum(II) catalyzed *trans*→*cis* olefin isomerization.

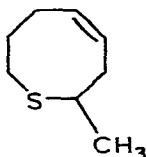
Results and discussion

cis-Thiacyclooct-4-ene complexes

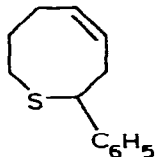
The unsaturated cyclic sulfides *cis*-thiacyclooct-4-ene (I, C₇H₁₂S) and the 2-substituted derivatives (II, C₈H₁₄S; III C₁₃H₁₆S) react with MCl₄²⁻ (M = Pd,



(I)



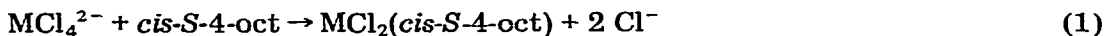
(II)



(III)

(*cis*-S-4-oct)

Pt) to form ivory (Pt) or yellow (Pd) complexes of the type MCl₂(*cis*-S-4-oct) in about 70–75% yields (eq. 1).



The products are monomeric in acetone and non conducting in nitrobenzene. The palladium complexes were also prepared from PdCl₂(C₆H₅CN)₂ by a general method already known for preparation of olefin derivatives of palladium(II) [7]. The mass spectra of the platinum derivatives, reported in Table 1, show the parent ions along with fragments corresponding to the loss of halide atoms; in all cases the C₄H₇S⁺ fragment generated from the olefin by electron impact was the base peak. The infrared spectra of the complexes indicate the absence of the bands at 1650 cm⁻¹ (C₈H₁₄S) and at 1649 cm⁻¹ (C₁₃H₁₆S) assigned to the >C=C< stretching frequency of the uncoordinated double bond. Our assignments of these new bands indicate reductions in frequency upon coordination (155–165 cm⁻¹ for platinum, 140–135 cm⁻¹ for palladium derivatives) which are larger than those observed for complexes of platinum or palladium with unsaturated phosphines or unsaturated open chain sulfides. If it is assumed that the reduction of the >C=C< stretching frequency is a measure of the strength of the M–olefin bond (and there is considerable doubt about this assumption [7]), the results indicate that the strength of the olefin coordination by the *cis*-thiacyclooct-4-ene ligands is significantly higher than that in the unsaturated phosphine or sulfide complexes. The bands in the region 310–340 cm⁻¹ in the chloro complexes of palladium and platinum are assigned as metal–chlorine stretching frequencies, and indicate mutually *cis*-chlorine atoms. Furthermore, the chelate derivatives react with CN⁻ to liberate the original bidentate ligands. From these observations the complexes are formulated as square planar chelate compounds of palladium(II) and platinum(II) with both the sulfur atom and the olefin double bond coordinated to the metal.

The *cis*-2-methylthiacyclooct-4-ene reacts with [PtCl₃(C₂H₄)]⁻ in acetone to afford PtCl₂(*cis*-C₈H₁₄S) in a 70% yield. In these reactions the cyclic olefin behaves as do other bidentate ligands (bipyridyl or ethylene diamine), and although no kinetic studies have been performed, the mechanism may be simi-

TABLE 1
ANALYTICAL AND SPECTRAL DATA FOR PLATINUM(II) AND PALLADIUM(II) COMPLEXES

Complex	M.p. °C (dec.)	Analysis (Found (calcd.) (%))				Infrared data (cm ⁻¹)		Mass fragments (m/e) ^a			Olefin [†]
		C	H	Cl	S	$\nu(\text{C}=\text{C})$	$\nu(\text{M}-\text{Cl})$	M ⁺	(M-2X) ⁺	(M-2X) ⁺	
PtCl ₂ (<i>cis</i> -C ₇ H ₁₂ S)	250-253	21.00 (21.03)	3.03 (3.07)	17.80 (17.99)	8.10 (8.13)	—	330, 310	400(394) ^b	—	—	—
PtCl ₂ (<i>cis</i> -C ₈ H ₁₄ S)	185-188	23.50 (23.54)	3.51 (3.46)	17.18 (17.37)	7.85 (7.85)	1485	380, 310	407 (12)	372 (10)	237 (3)	142 (85)
PdCl ₂ (<i>cis</i> -C ₆ H ₁₄ S)	170-173	29.30 (30.07)	4.35 (4.42)	22.10 (22.19)	10.00 (10.03)	1510	325, 305	—	—	327(319) ^b	—
PtCl ₂ (<i>cis</i> -C ₁₃ H ₁₆ S)	195-198	33.56 (33.20)	3.50 (3.43)	15.18 (15.05)	6.80 (6.82)	1495	340, 320	469 (6)	434 (7)	399 (3)	204 (69)
PdCl ₂ (<i>cis</i> -C ₁₃ H ₁₆ S)	190-195	41.50 (40.91)	4.36 (4.22)	18.71 (18.58)	8.51 (8.40)	1515	335, 310	—	—	—	—
PtBr ₂ (<i>cis</i> -C ₁₃ H ₁₆ S)	205-208	28.22 (27.92)	2.96 (2.88)	—	5.80 (5.73)	1490	235, 215	557 (4)	478 (5)	399 (8)	204 (80)

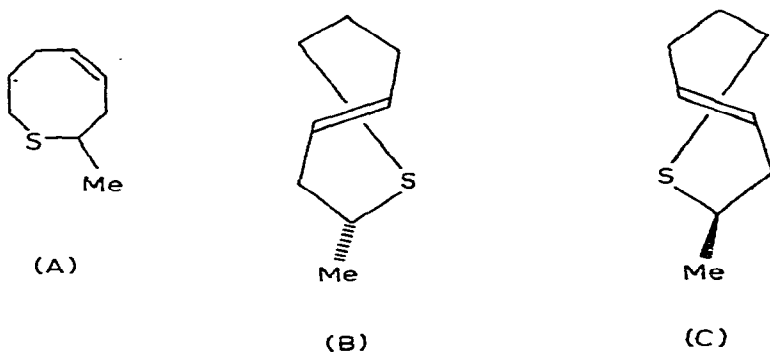
^a Referred to the most abundant isotopes, relative intensities are given in parentheses and are calculated on C₄H₇S⁺ fragment (100%). ^b Molecular weight from osmometric measurements in acetone.

lar to that found in the reaction between Zeise's salt and bipyridyl [8], involving an unstable $[\text{PtCl}(\text{C}_2\text{H}_4)(\text{C}_8\text{H}_{14}\text{S})]^+$ intermediate which rapidly rearranges to the thermodynamically stable $\text{PtCl}_2(\text{C}_8\text{H}_{14}\text{S})$ derivative. Attempts to isolate the cationic intermediate species or thiacyclooct-4-ene bridged complexes, corresponding with those found in the reaction between Zeise's salt and ethylenediamine [9], were unsuccessful.

Reactions of the platinum complexes with some unidentate ligands such as *p*-toluidine or triphenylphosphine replace the whole chelating unsaturated cyclic sulfide. This behaviour contrast with the observation that these unidentate donor ligands will substitute only one coordination site, the olefinic double bond, in dichloropent-4-enyldimethylarsineplatinum(II) [10], and may be indicative of the lower stability of $\text{PtCl}_2(\text{cis-S-4-oct})$ complexes with respect to unsaturated arsine or phosphine derivatives.

trans-cis-Thiacyclooct-4-ene isomerization

Attempts were also made to bring about coordination of the eight-membered cyclic olefins in their *trans* form with the aim at producing a simple chemical method for separation of the *cis* from the *trans* isomers. For this purpose reaction 1 was carried out with mixtures of the three cyclic sulfides A, B and C in which the two *trans* olefins, B and C, are diastereoisomers arising from the presence in the molecule of two elements of chirality. One is the chiral center at C(2) the second is a chiral plane; the diastereoisomers derive their stability from restricted conformational inversion*.



When Na_2PtCl_4 and A (41%), B (52%), C (7%) was treated in *n*-propanol with a molar ratio $\text{PtCl}_4/\text{total olefin}$ of 1/1 (case a) or 1/10 (case b) a white precipitate was immediately formed. Analytical and spectral data showed this to be the $\text{PtCl}_2(\text{cis-C}_8\text{H}_{14}\text{S})$ adduct**. The *cis* nature of the coordinated olefin was established from the following observations:

- (1) Treatment of the isolated complex with CN^- liberates A.
- (2) GLC analyses of the reaction mixture, after separation of the complex, reveals the absence of *trans* olefins (A and B) moreover, further $\text{PtCl}_2(\text{cis-C}_8\text{H}_{14}\text{S})$ can be obtained from the same solution (case b).
- (3) Preliminary results of an X-ray determination on the $\text{PtCl}_2(\text{C}_8\text{H}_{14}\text{S})$ deriv-

* For separation and configurational assignment of these isomers see ref. 11.

** Similar results were obtained with mixtures of *cis*- and *trans*-thiacyclooct-4-ene and Zeise's salt.

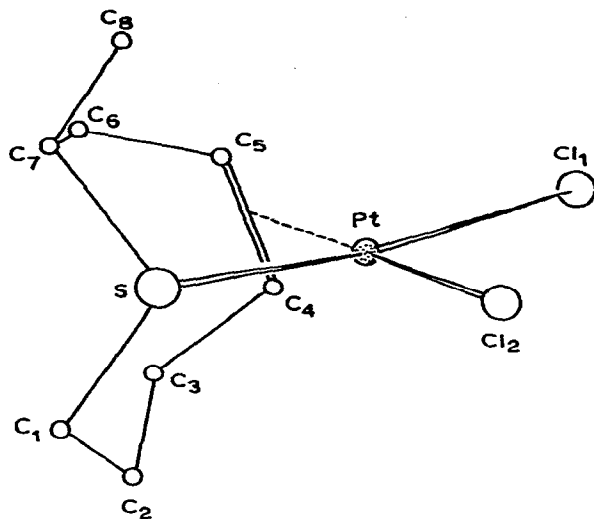


Fig. 1.

ative obtained from the above preparation indicates that the 2-methylthiacyclooct-4-ene is bonded through the sulphur atom and the *cis* double bond to the square-planar platinum atom (Fig. 1). This excludes the possibility of a *trans* → *cis* conversion during displacement (reaction with CN^-) of the eventually coordinated *trans*-olefin, as recently found for the stoichiometric *cis* → *trans* isomerization in the substitution of ethyl propenyl ether from *trans*-[PtCl₂(*cis*-CH₃CH=CHOC₂H₅)Py] with pyridine [12].

It is noteworthy that, owing to coordination, the *cis*-2-methylthiacyclooct-4-ene ligand can no longer undergo conformational inversion and add a further element of chirality, the sulfur atom, to the chiral center at the C(7) carbon atom which bears the methyl group (see Fig. 1). Thus two diastereoisomers are likely to be produced in the preparation of PtCl₂(*cis*-C₈H₁₄S) derivative. In one of these the CH₃ group is on the same side as the platinum atom (D), and in the other the CH₃ is on the opposite side of the platinum atom (E) (Fig. 2).

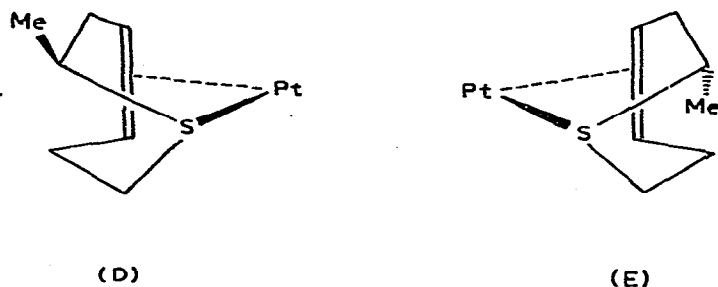


Fig. 2.

The X-ray structural determination, together with the observation that TLC on the reaction mixture indicated the presence of only one product, indicate that the E isomer is disfavoured, in the formation of the complex, probably for steric reasons.

The evidence reported above clearly indicates that the *trans*-thiacyclooct-4-ene complexes of platinum cannot be obtained in accord with the observation that *cis* olefins generally give more stable metal olefin complexes than the corresponding *trans* isomers [13]. Moreover since the *trans*→*cis* olefin isomerization occurs at room temperature and goes to completion in a few minutes in the presence of platinum derivatives, whereas the *trans* isomers (B and C) undergo irreversible thermal conversion to the thermodynamically more stable *cis* olefin upon heating at 100°C for several hours [11], it is suggested that platinum(II) derivatives catalyze the *trans*→*cis*-thiacyclooct-4-ene isomerization. Furthermore, the isolation of *cis*-2-methylthiacyclooct-4-ene as the sole olefin product (GLC analyses) from the reaction of $\text{PtCl}_2(\text{cis-C}_8\text{H}_{14}\text{S})$ and a mixture of *cis* and *trans* sulfides, suggests that the catalysis must be ascribed to the thiacyclooct-4-ene olefin complexes.

A detailed examination of these unusual catalyzed isomerizations is currently in progress.

Experimental

Reagent grade solvents were dried over molecular sieves. Hexane and diethyl ether were distilled from sodium and n-propanol from CaO. $[\text{PtCl}_3(\text{C}_2\text{H}_4)]\text{K}$ and $\text{PdCl}_2(\text{C}_6\text{H}_5\text{CN})_2$ were prepared by standard methods. GLC analyses were carried out with a Hewlett-Packard 5700 gas chromatograph equipped with flame ionization detector. Conductivities were measured on 10^{-3} solutions in nitrobenzene with a LKB 5300B conductivity bridge. Infrared spectra were recorded on a Perkin-Elmer 180 spectrophotometer; mass spectra were measured on a JEOL JMS-D100 instrument with a nominal beam energy of 70 eV. Molecular weights were determined osmotically.

Preparation of $\text{PtCl}_2(\text{cis-S-4-oct})$ (S-4-oct) = thiacyclooct-4-ene, ($\text{C}_7\text{H}_{12}\text{S}$), 2-methylthiacyclooct-4-ene ($\text{C}_8\text{H}_{14}\text{S}$) and 2-phenylthiacyclooct-4-ene ($\text{C}_{13}\text{H}_{16}\text{S}$)

These complexes were prepared by the procedure described below for $\text{PtCl}_2(\text{cis-C}_8\text{H}_{14}\text{S})$, starting both from (a) Na_2PtCl_4 and (b) $[\text{PtCl}_3(\text{C}_2\text{H}_4)]\text{K}$.

(a) To a stirred solution of 0.150 g (1.06 mmol) of $\text{C}_8\text{H}_{14}\text{S}$ in 20 ml of n-propanol were added 0.404 g (1.06 mmol) of Na_2PtCl_4 dissolved in the minimum amount of the same solvent. An ivory precipitate was formed immediately. After 1 h the ethyl ether was added to complete the precipitation. The solid was filtered off, washed with small amount of water, n-propanol and ethyl ether, and dried in vacuo and recrystallized from $\text{CH}_2\text{Cl}_2/\text{n-hexane}$ (75% yield).

(b) To a solution of 0.106 g (0.75 mmol) of *cis*- $\text{C}_8\text{H}_{14}\text{S}$ in 20 ml of acetone the stoichiometric amount of $[\text{PtCl}_3(\text{C}_2\text{H}_4)]\text{K}$ in acetone was added dropwise with stirring. After 1 h ethyl ether was added to the solution, and the precipitate purified as described above (70% yield).

Preparation of $PtBr_2(cis-C_{13}H_{16}S)$

The complex was prepared in a 80% yield from Na_2PtBr_4 and 2-phenylthia-cyclooct-4-ene by the procedure described for the chloro derivatives.

Preparation of $PdCl_2(cis-C_8H_{14}S)$

0.144 g (1.01 mmol) of *cis*- $C_8H_{14}S$ was treated in CH_2Cl_2 with an equimolar amount (0.389 g) of $PdCl_2(C_6H_5CN)_2$. After 2 h the yellow solution was filtered and its volume reduced to about 5 ml. Addition of ethyl ether gave 0.173 g (58% yield) of yellow $PdCl_2(cis-C_8H_{14}S)$.

Preparation of $PdCl_2(cis-C_{13}H_{16}S)$

The complex was prepared in a 65% yield from $(NH_4)_2PdCl_4$ and the stoichiometric amount of *cis*- $C_{13}H_{16}S$ in acetone. The $PdCl_2(cis-C_{13}H_{16}S)$ derivative was purified as described for the platinum analogue.

Reactions of $PtCl_2(cis-S-4-oct)$ with unidentate ligands

To a solution of $PtCl_2(cis-S-4-oct)$ in CH_2Cl_2 (20 ml) was added a slight excess of $P(C_6H_5)_3$. After 2 h the solution was evaporated to dryness under reduced pressure and the resulting white solid was washed with hexane and identified as *cis*-dichlorobis(triphenylphosphine)platinum. (Found: C, 55.1; H, 3.9. $C_{36}H_{30}Cl_2P_2Pt$ calcd.: C, 54.7; H, 3.8%. $\nu(Pt-Cl)$ at 315 and 290 cm^{-1}). Similarly prepared was *cis*-dichlorobis(*p*-toluidine)platinum. (Found: C, 34.9; H, 3.8. $C_{14}H_{18}Cl_2N_2Pt$ calcd.: C, 35.0; H, 3.75%. $\nu(Pt-Cl)$ at 342 and 320 cm^{-1}).

Reaction of $PtCl_2(cis-S-4-oct)$ with CN^-

A thiacyclooct-4-ene complex was suspended in water and treated with excess KCN. After 15 min the solution was shaken with CH_2Cl_2 and the organic layer was dried over $CaCl_2$ and concentrated under reduced pressure. In the case of liquid cyclic sulfides ($C_7H_{12}S$ and $C_8H_{14}S$) GLC showed the presence of the displaced *cis*-*S*-4-*oct* in the case of the solid olefin $C_{13}H_{16}S$, its formation was confirmed from its mass spectrum (parent ion *m/e* 204).

Reaction of Na_2PtCl_4 with *trans*- and *cis*-2-methylthiacyclooct-4-ene

To a stirred *n*-propanol solution containing 0.103 g (0.725 mmol) of a mixture of *cis*- and *trans*-2-methylthiacyclooct-4-ene (0.29 mmol *cis* and 0.435 mmol of total *trans* isomers) were added 0.022 g (0.058 mmol 20% with respect to the *cis* isomer) of Na_2PtCl_4 . After 1 h diethyl ether was added to complete the precipitation of the formed $PtCl_2(cis-C_8H_{14}S)$, which was separated by filtration (0.015 g, 65% yield based on Na_2PtCl_4). GLC analyses of the filtrate showed that only *cis*- $C_8H_{14}S$ was present, and addition of an excess of Na_2PtCl_4 produced additional $PtCl_2(cis-C_8H_{14}S)$ (0.191 g), which increased the yield to about 70% based on total olefin. When the same experiment was carried out with an equimolar amount of Na_2PtCl_4 and a mixture of *cis* and *trans* (2/3) olefins the $PtCl_2(cis-C_8H_{14}S)$ was obtained in 70% yield.

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