

## STEREOCHEMISTRY OF OLEFINS—VIII

### DETERMINATION OF THE ABSOLUTE CONFIGURATION OF SQUARE PLANAR COMPLEXES

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**Abstract**—Assignment of stereochemistry using the d-d transitions of platinum (II)-olefin complexes has been developed and a quadrant rule evolved. The treatment has been applied to complexes of both mono- and di-olefins. In an appendix possible extension of this concept to palladium complexes is indicated.

IT HAS been shown that the CD data of a wide variety of olefins have proved amenable to interpretation by the octant rule.<sup>1a</sup> During the development of these studies it became apparent that assignment of the appropriate transition in the  $\pi$ - $\pi^*$  region (upon which successful operation of the rule depends) could, on occasion, prove troublesome.<sup>1b, c</sup> In order to provide additional verification of stereochemical assignment, attention was directed to the possibility of obtaining and interpreting the chiroptical properties of a range of chromophoric derivatives. To fulfil a useful role, such derivatives should possess electronic absorption bands far removed from the olefin transitions (preferably in the visible region), should be easily formed, and should be amenable to recovery of the original olefin, this last factor being of great importance for natural product studies. Such a derivative would not only provide an interesting optically active chromophore in its own right, but could frequently be useful to avoid instrumental and/or overlapping chromophoric problems which arise in the spectra of natural products.

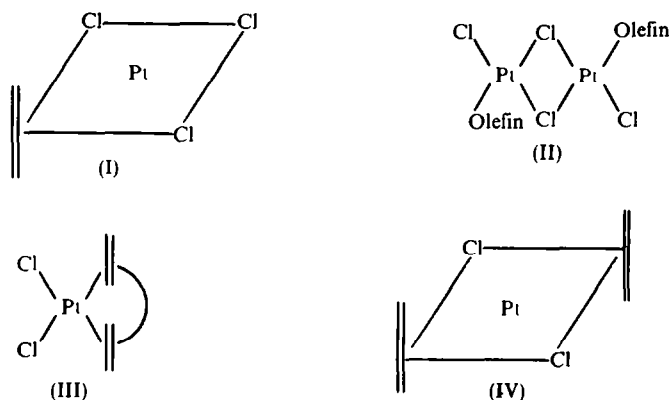
The complexes of transition metals with olefins often display absorption bands which in the case of Pt(II) are optically active.<sup>2</sup> The transitions of these square planar complexes have been assigned to the *d-d* bands of the metal and it was anticipated that, by analogy with octahedral complexes, the absolute stereochemistry of the complex (and hence the olefin) could be deduced.<sup>3</sup>

Other metals were considered for this purpose.<sup>4</sup> Divalent Pt and Pd form the most stable olefin complexes,<sup>5</sup> Ag(I)<sup>6</sup> and Au(I)<sup>7</sup> complexes tend to dissociate in solution and are usually colourless, whilst those derived from Rh(I), [ $d^8$ ; isoelectronic with Pd(II)] are usually coloured but present stability problems, especially in halogenated solvents.<sup>8</sup> On balance we elected to study Pt(II) and Pd(II) complexes.

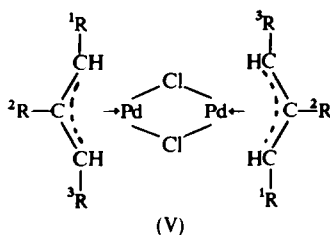
Although the complexing power of platinum(II) for ethylene has been appreciated for a long time<sup>9</sup> it is only comparatively recently that the bonding situation has been studied systematically.<sup>10</sup> Thus Type I complexes (Fig. 1) may be formed by displacement of one of the chlorine atoms of the tetrachloroplatinate ion to give a singly charged anion, which in turn may be dimerized to the uncharged species (Type II).<sup>11</sup>

† Part VII M. Fetizon, I. Hanna, T. Devon, A. I. Scott and A. D. Wrixon, *Chem. Comm.*, 1971 in press.

In the case of nonconjugated dienes, in particular 1,5-dienes, displacement of two chlorine atoms leads to the uncharged chelate (Type III).<sup>12</sup> Such chelates are formed by 1,5-cyclooctadiene, dicyclopentadiene, and dipentene (*R*, *S*-limonene). *Trans*-bis monoolefin complexes (Type IV) have been described<sup>13</sup> but are usually stable only at low temperature. The four classes are shown below.



With Pd(II), Types II and III complexes are formed in some cases.<sup>14</sup> However the Pd Type II complexes are less stable than the Pt counterparts<sup>15</sup> and dipentene does not form a Type III Pd(II) complex.<sup>14</sup> There is also a tendency for allylic elimination of hydrogen to form stable Pd  $\pi$ -allyl complexes (Type V), the corresponding Pt-allyl system being authenticated but rare.<sup>16, 17</sup>

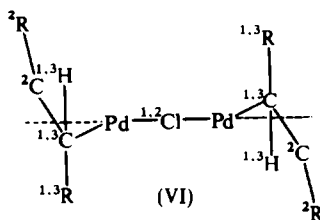


Thus for the task in hand our interest has centred on the Pt(II) complexes of Types I–III and the Pd(II) complex of Type V. A fortuitous outcome of this approach was the finding that in several cases failure to detect CD bands in one class of complex was offset by the appearance of optically active d–d transitions in one of the other complex types.

The concepts of the bonding in these complexes were laid down by Dewar<sup>18</sup> for the case of the Ag(I)-olefin series and by the classic work of Chatt and Duncanson<sup>19</sup> on Zeise's salt, where the idea of  $\pi$  donation and d-orbital back-bonding were developed. These structural proposals have been confirmed and refined by X-ray diffraction data<sup>20–22</sup> which showed that the plane of the olefinic C=C bond is perpendicular to the Pt square plane. The C–C bond is lengthened by coordination to a distance corresponding to a position between that of a C–C single and double bond. Carbon

substituents are displaced somewhat from coplanarity with the olefinic carbon atoms by repulsion from Pt or through adoption of some  $sp^3$  character.<sup>19, 23</sup> Other evidence has been adduced for the retention of much of the olefinic character on complexation.<sup>24</sup>

In the case of Pd  $\pi$ -allyl complexes structures of Type VI have been demonstrated by X-ray diffraction analysis,<sup>25, 26</sup> where the plane defined by the three allyl carbon atoms is oriented at an angle of  $125^\circ$  to the Pd-Cl-coordination plane. A substituent on  $C_2$  is inclined from the allyl plane towards the Pd atom.



#### Optical Activity of Platinum Olefin Complexes

An acyclic, achiral olefin may be prochiral with respect to coordination and this effect was demonstrated<sup>27</sup> with the Pt complex of propylene, the substituted carbon ( $C^*$ ) becoming asymmetric on coordination. The appropriate *R* and *S* configurations



are shown in VII and VIII respectively.<sup>28</sup> With the Pt(II) complex of *trans*-2-butene, two asymmetric centres with the same chiralities are produced, whilst with *cis*-2-butene the chiralities are opposed and a *meso* situation is reached.<sup>27</sup>

By further coordination with optically active  $\alpha$ -methylbenzylamine either *trans* (IX)<sup>27</sup> or *cis* (X)<sup>29</sup> on the Pt square plane (with respect to the complexed olefin) resolution of the diastereoisomers was achieved. In the case of the *trans*-2-butene *trans* complex (as IX) the amine may be removed after resolution to give the optically active  $[PtCl_3(olefin)]^- [(NH_3)_4Pt]^+ Cl$  salt. The sign of  $[\alpha]_D$  of the latter complex was found to be the same as that of the corresponding *trans*-amine complex (IX).<sup>27</sup>

At the outset of this work we were guided by a CD study of the *cis*-complexes [as (X)] which indicated that the configuration of the olefin is most probably reflected in the first *d-d* transition near 370 nm and further that (*-*)-*trans*-cyclooctene formed a dextrorotatory *cis* complex with *S*-amine.<sup>2, 27</sup>



We chose as initial compounds for ORD and CD work the resolved diastereoisomers of the *trans* amine complexes of the *trans*-cycloolefins containing 8, 9 and 10 membered rings.<sup>30, 31</sup> The appropriate spectra are shown in Figs. 1-5.

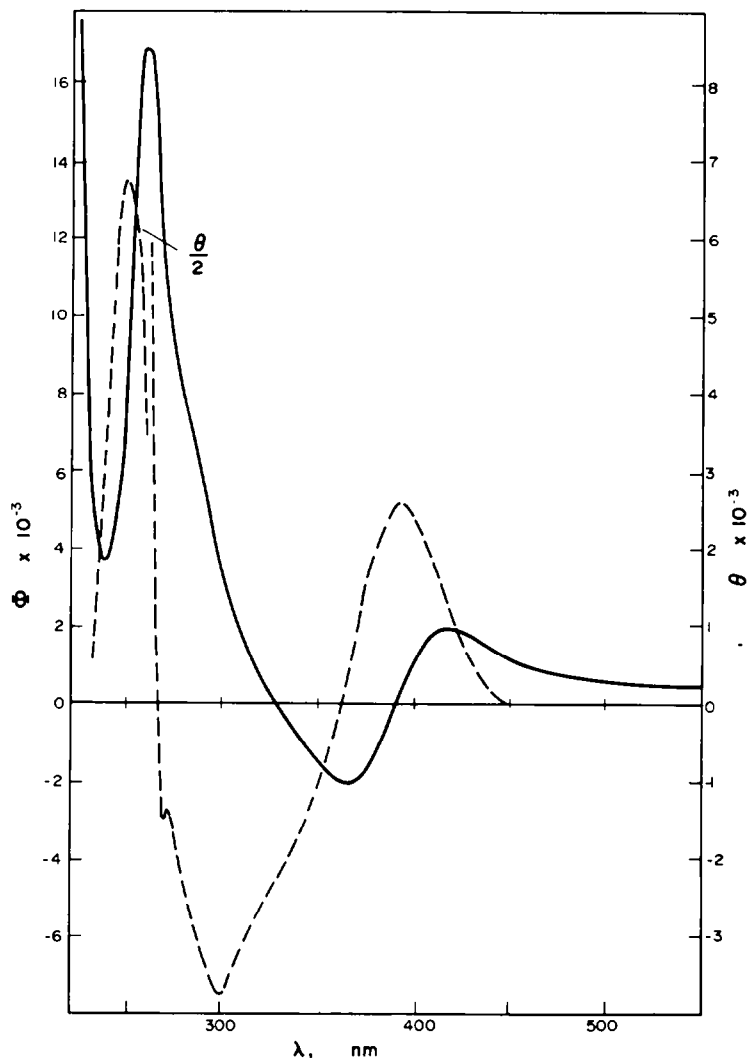


FIG 1. ORD ————— and CD - - - - - spectra of (+)*trans*-dichloro-(*trans*-cyclooctene)-(R)-(α-methylbenzylamine) Pt II in  $\text{CH}_2\text{Cl}_2$ .

The starting point for our correlations was (*R*)(-)*trans*-cyclooctene whose absolute configuration was defined by Cope using a chemical method.<sup>32</sup> This enantiomer was obtained from the less soluble dextrorotatory (*R*)-amine olefin complex. When *trans*-cyclononene was liberated from the corresponding Pt-amine complex racemisation was rapid ( $t_{\frac{1}{2}} \approx 4$  min.), whilst no optical activity could be observed in a specimen of *trans*-cyclododecene prepared in analogous fashion.

However, comparison of the ORD and CD spectra of (+)-*trans*-dichloro (*trans*-cyclooctene) (*R*)-( $\alpha$ -methylbenzylamine Pt(II)) (Fig. 1) and of the less soluble complex (+)-*trans*-dichloro-(*trans*-cyclodecene)-(*R*) ( $\alpha$ -methylbenzylamine) Pt(II) (Fig. 2) clearly indicates that the same absolute configuration (*S, S*) obtained for the coordinated olefinic centres in both complexes.<sup>†</sup>

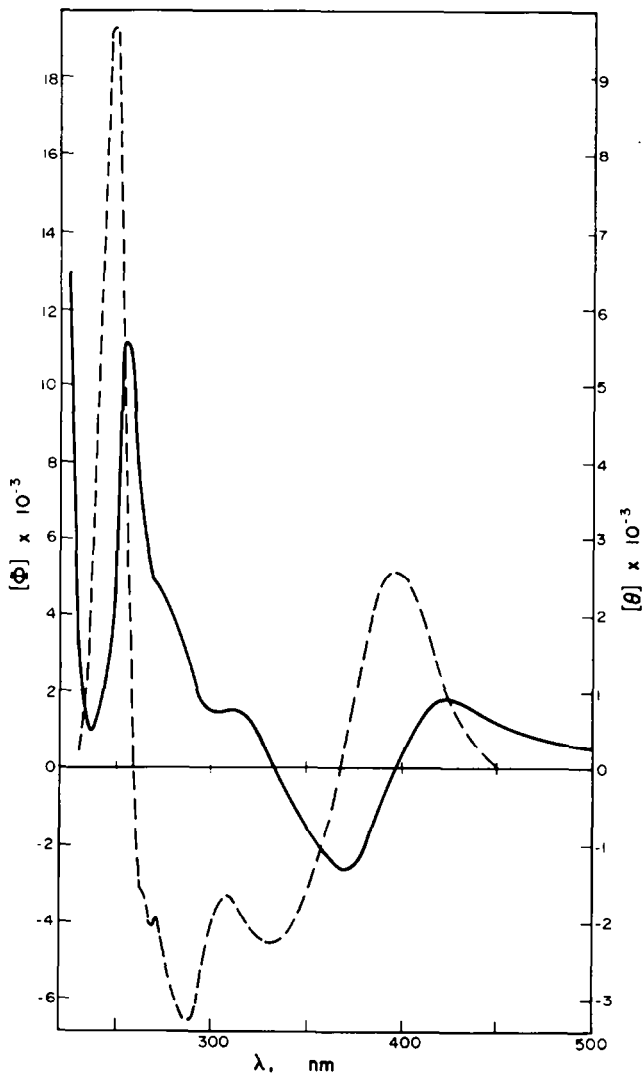


FIG. 2. ORD ————— and CD - - - - - spectra of (+)*trans*-dichloro-(*trans*-cyclodecene)-(*R*)-( $\alpha$ -methylbenzylamine) Pt II in  $\text{CH}_2\text{Cl}_2$ .

<sup>†</sup> It is important to note that a dissymmetric cycloolefin of absolute stereochemistry (*R*) will, on complexation with Pt, display the stereochemistry *S, S* at the coordinated olefinic centres as a result of the priority rule.<sup>28</sup>

Similarly, the ORD and CD curves of  $(-)$ -*trans*-dichloro-(*trans*-cyclononene)- $(S)$ -( $\alpha$ -methylbenzylamine) Pt(II) (Fig. 3) are antipodal to those of Figs. 1 and 2 requiring the  $\underline{R}$ ,  $\underline{R}$  configuration in the ligand and hence the  $\underline{S}$ -configuration for the

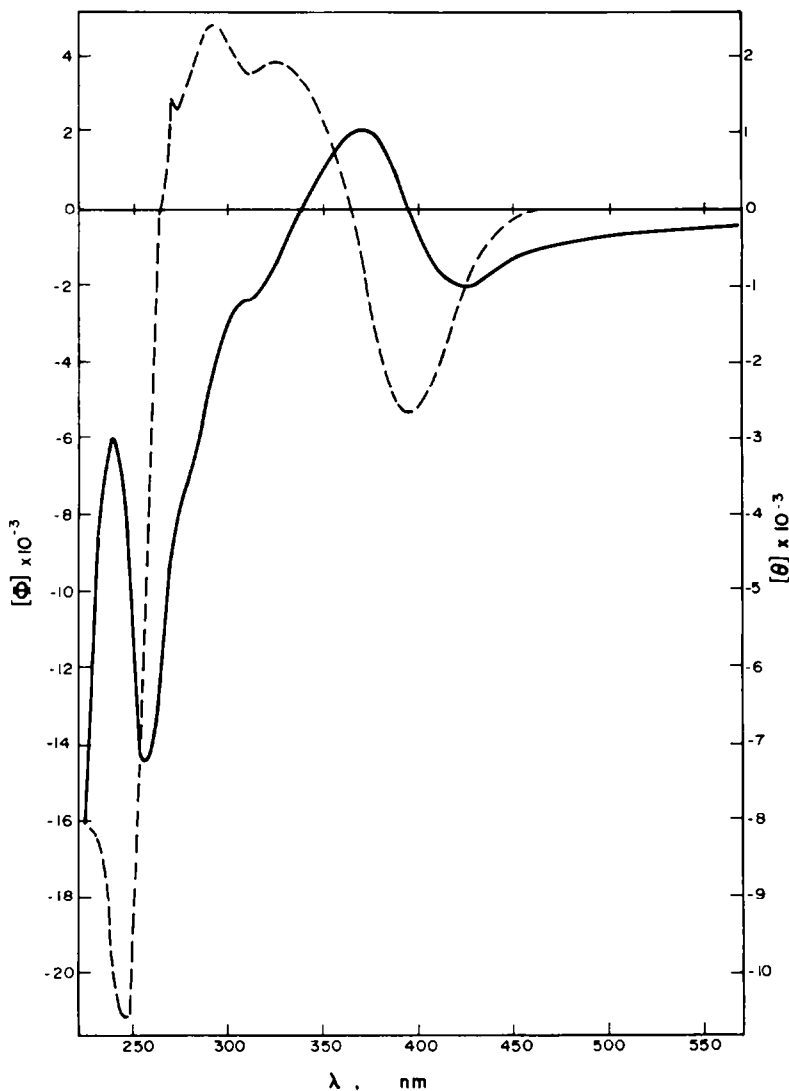


FIG. 3. ORD ————— and CD - - - - - spectra of  $(-)$ -*trans*-dichloro-(*trans*-cyclononene)- $(S)$ -( $\alpha$ -methylbenzylamine) Pt II in  $\text{CH}_2\text{Cl}_2$ .

liberated but transient  $(+)$ -*trans*-cyclononene.<sup>31, 32</sup> With  $(+)$ -*trans*-dichloro-(propylene)- $(R)$ -( $\alpha$ -methylbenzylamine) platinum(II), the rotational strength is (as expected) somewhat reduced in magnitude but again, a positive Cotton Effect allows the assignment of the  $\underline{S}$  configuration to the olefin centre.

*Optically active amine contribution*

The possible contribution of the optically active amine to the lowest energy transition was examined (Fig. 4) and it was found that the sign of the first *d-d* transition is

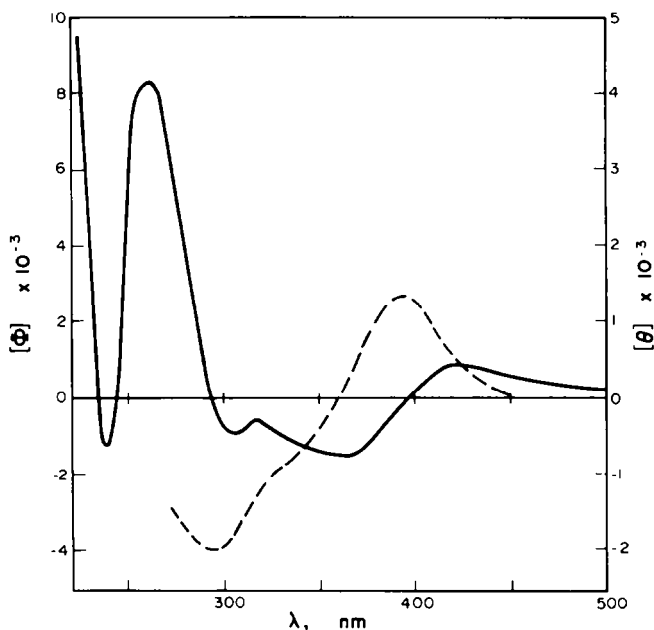


FIG 4. ORD ————— and CD ········· spectra of (+)*trans*-dichloro-(*trans*-cyclooctene)-(S)-(α-methylbenzylamine) Pt II in  $\text{CH}_2\text{Cl}_2$ .

unaltered by a change in the configuration (*R*) amine  $\rightarrow$  (*S*) amine for the (–)*R*-*trans*-cyclooctene complex (the complex with the (*S*) amine is the more soluble diastereoisomer obtained by Cope).<sup>30</sup> Although a shift to longer wavelength is observed in di- $\mu$ -chloro-1,3-dichloro-2,4-bis-(–)*trans*-cyclooctene]-diplatinum(II) (see Type II above and Fig. 5), the magnitude and sign of the ORD and CD spectra are virtually unaffected by complete removal of the ligand amine.

Difficulty was experienced in preparing a pure sample of *trans*-dichloro-(ethylene)-(*R*)-(α-methylbenzylamine) platinum(II) due to the presence of a persistent impurity which was possibly formed by chelation of the amine through  $\sigma$  bonding of the aromatic ring to platinum.<sup>33</sup> However measurements showed that the long wavelength band at about 400 nm was only weakly optically active ( $[\theta] = 50$ ). This is to be expected for an optically active monodentate ligand with almost free rotation of the ligand. A similar order of magnitude was obtained when *d*-amphetamine (which affords a more readily purified complex) was used as the optically active amine. These results are also consistent with the measurements previously made on the *cis*-amine olefin complexes,<sup>2</sup> where again the long wavelength optically active transition possesses almost negligible rotational strength when the olefin is ethylene or *cis*-2-butene.

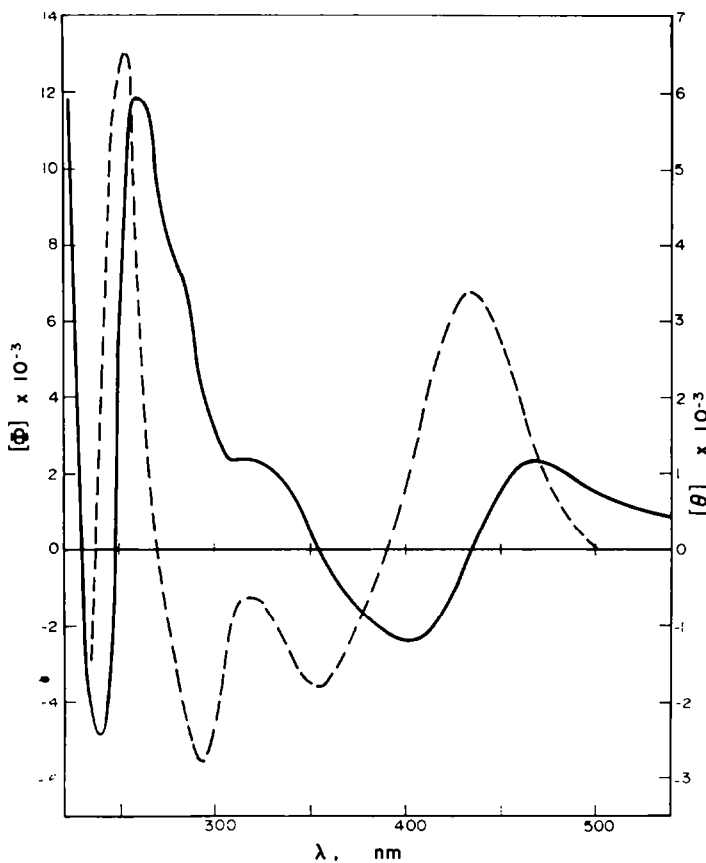


FIG 5. ORD ————— and CD - - - - - spectra of (+) di- $\mu$ -chloro-1,3-dichloro-2,4-bis-(*trans*-cyclooctene)diplatinum II in  $\text{CH}_2\text{Cl}_2$ .

#### *cis*-Amine olefin complexes

An X-ray analysis<sup>34</sup> of (-)-*cis*-dichloro-(*trans*-2-butene-(S)-( $\alpha$ -methylbenzylamine) platinum(II) has shown the R, R configuration for the olefinic carbons. This compound exhibits a negative long wavelength CD band at about 370 nm.<sup>2</sup> (+)-*Trans*-cyclooctene with the S absolute configuration (and, therefore R, R when coordinated to platinum) produces a levorotatory *cis* complex when the S amine is used.<sup>27</sup>

These results suggest that the sign of the Cotton Effect of the lowest energy *d-d* transition of platinum is independent of both the presence of the optically active amine and the relative positions of the amine and olefin on the square plane of Pt and further that this transition reflects the absolute configuration of the coordinated olefin. Thus when the olefin carbons assume the R, R-configuration on coordination, negative long wavelength Cotton Effect results and with the S, S configuration a positive Cotton Effects results. This can be more readily described in terms of a local Quadrant Rule<sup>35</sup> (see Fig. 6).



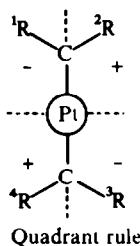


FIG 6. Quadrant Rule for Pt-olefin complexes giving sign of the long wavelength Cotton Effect. For simple mono- and *trans*-disubstituted olefins a positive Cotton Effect indicates the  $\underline{S}$  configuration for the coordinated olefin centres and a negative Cotton Effect the  $\underline{R}$  configuration.



FIG 7. Quadrant projections for (a) ( $\underline{R}$ ) *trans*-cycloalkenes and (b) (+) propylene and (+) *trans*-2-butene complexes of Pt. The complexed olefin carbon centres possess the  $\underline{S}$  absolute configuration (positive long wavelength Cotton Effect).

The chirality of the complexed olefinic carbon centres is related to the location of substituents in quadrants of alternating sign formed by the intersection of the Pt square plane and the vertical plane normally corresponding to the olefinic C—C double bond<sup>20, 21, 22</sup> viewed along the Pt x-axis. The quadrant diagrams for (a) the ( $\underline{R}$ )-*trans*-cycloalkenes, (b) (+) *trans*-2-butene and (+) propylene (*cis* or *trans*-amine) complex are shown in Fig. 7. Since our preliminary communications<sup>35</sup> the Quadrant rule has been used to deduce the absolute conformation of the corresponding (+) but-1-ene complex, a result further substantiated by X-ray diffraction.<sup>36</sup>

Recently<sup>37</sup> the resolution method of Cope<sup>30</sup> has been applied to *trans*-bicyclo [8.2.2] tetradeca-5,10,12,13-tetraene. Using ( $\underline{R}$ )- $\alpha$ -methylbenzylamine as the resolving amine, (–)-*trans*-dichloro-(*trans*-bicyclo [8.2.2] tetradeca-5,10,12,13-tetraene)-( $\underline{R}$ )-( $\alpha$ -methylbenzylamine) platinum II was obtained as the less soluble diastereoisomer. The ORD and CD spectra of this compound (Fig. 8) showed a negative long wavelength Cotton Effect at about 400 nm. Using the Quadrant Rule (Fig. 9) the  $\underline{R}$ ,  $\underline{R}$  configuration for the coordinated olefin is thus demonstrated. The less soluble diastereoisomer obtained with ( $\underline{S}$ )- $\alpha$ -methylbenzylamine exhibited antipodal ORD and CD spectra indicating the  $\underline{S}$ ,  $\underline{S}$  configuration for the coordinated olefin.

#### Application of the quadrant rule to other optically active olefins

With optically active steroid or terpenoid olefins, resolution of diastereoisomeric complexes created by the prochiral olefin faces is unnecessary. Preferential coordination to one side of the double bond will normally occur automatically owing to the differing steric requirements of either side.

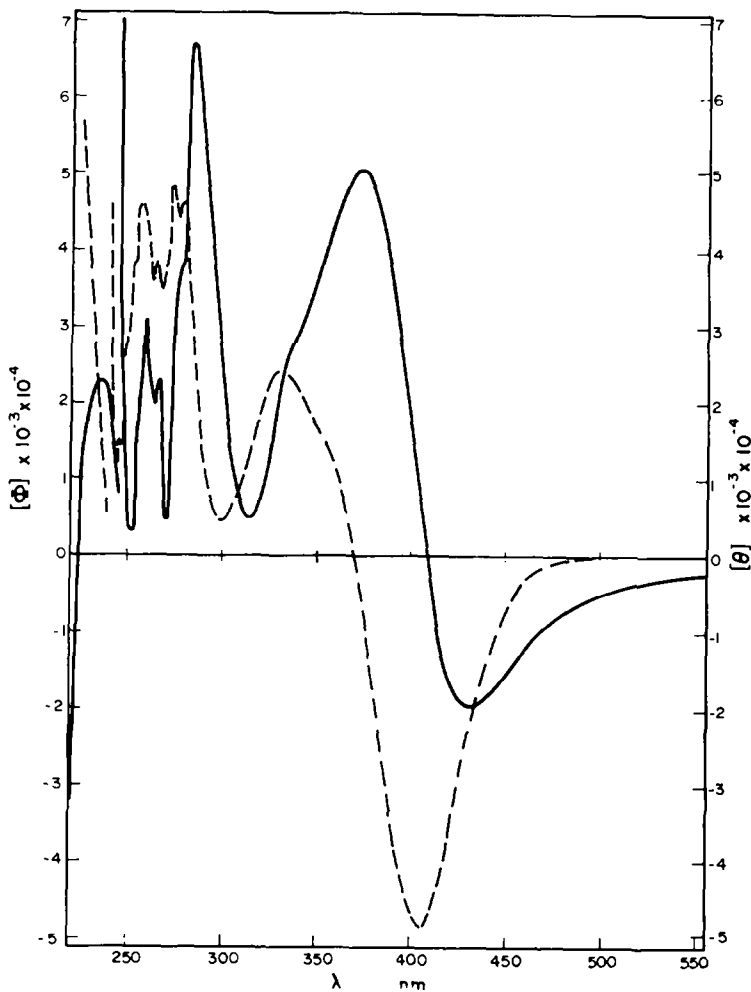
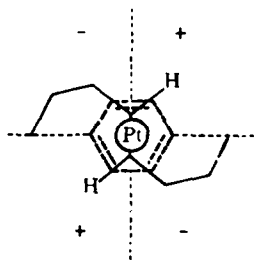


FIG 8. ORD ——— and CD - - - - - spectra of (-) *trans*-dichloro-(*trans*-bicyclo [8,2,2] tetradeca-5,10,12,13-tetraene)-(R)-(α-methylbenzylamine) Pt II in  $\text{CH}_2\text{Cl}_2$ .



Quadrant projection

FIG 9. Quadrant projection for (-) *trans*-dichloro-(*trans*-bicyclo[8,2,2]tetradeca-5,10,12,13-tetraene)-(R)-(α-methylbenzylamine) Pt II.

Difficulty was experienced in the preparation of solid Pt complexes of such high molecular weight olefinic materials and thus a qualitative method was developed whereby the CD spectrum of an olefin dissolved in approximately 0.0025M alcoholic solution of sodium tetrachloroplatinate was measured after about 20 hr. This period of time was found to be generally the most useful, since it was sufficient for appreciable complexation to occur without the disadvantage of substantial decomposition. Since no solid complexes were obtained for these mono-olefins, it is probable that they exist as Type I anionic species. This is in good agreement with the observed UV spectra which were similar to that of Zeise's salt.<sup>38</sup>

The results for the long wavelength band of a number of optically active olefins complexed to Pt are given in Tables 1–3. Representative CD spectra with ellipticities calculated from the quantity of sodium tetrachloroplatinate used (excess olefin was always present) are given in Fig. 10.

TABLE 1. CD SPECTRA (LONG WAVELENGTH BAND) OF SOLUTIONS OF OPTICALLY ACTIVE MONOTERPENE OLEFINS IN 0.0025M ALCOHOLIC Na<sub>2</sub>PtCl<sub>4</sub> SOLUTION AFTER 20 HOURS

No	Compound	$\Delta\epsilon$	$\lambda_{\max}$ nm	Predicted sign
1	(-) $\beta$ -pinene	-0.016	440	+
2	(+) $\alpha$ -pinene	-0.01	450	-
3	(-) $\alpha$ -pinene	+0.01	430	+
4	(+) sabinene	-0.084	430	?
5	(+) sabinol	+0.018 -0.09	480 430	?
6	(+) <i>trans</i> -pinocarveol	+0.03	440	?
7	(+) camphene	No detectable C.D.		
8	(-) $\alpha$ -fenchene	+0.036	430	+
9	(+) $\beta$ -fenchene	-0.104	430	-
10	(-) car-3-ene	No detectable C.D.		

Where CD bands were detected, the first transition usually occurred at about 430 nm in a region somewhat analogous to that for di- $\mu$ -chloro-1,3-dichloro-2,4-bis[(-)-*trans*-cyclooctene] diplatinum(II) (Fig. 5). It is thus assumed that this long wavelength transition is identical to that observed with the *trans*-cycloalkene complexes.

Larger ellipticities were generally obtained with disubstituted olefins, while the complexes of trisubstituted olefins possessed reduced rotational strengths. As yet no

TABLE 2. CD SPECTRA (LONG WAVELENGTH BAND) OF SOLUTIONS OF OPTICALLY ACTIVE DITERPENE OLEFINS IN 0.0025M ALCOHOLIC Na<sub>2</sub>PtCl<sub>4</sub> SOLUTION AFTER 20 HOURS

No	Compound	$\Delta\epsilon$	$\lambda_{\max}$ nm	Predicted sign
11	phylocladene	+0.072	440	+
12	iso-phylocladene	+0.024	440	?
13	3-hydroxy-(-)-kaurene	+0.042	440	+
14	7-hydroxy-kaurenolide	+0.066	440	+
15	hirsutic acid C	-0.118	440	-
16	gibberlic acid	+0.04	430	+

Cotton Effects have been found for complexes of tetra-substituted double bonds, although the UV spectrum in a number of such cases has indicated complexation (e.g. nos. 33, 37 and 39; Table 3).

TABLE 3. CD SPECTRA (LONG WAVELENGTH BAND) OF SOLUTIONS OF OPTICALLY ACTIVE STEROIDAL OLEFINS IN 0.0025M ALCOHOLIC  $\text{Na}_2\text{PtCl}_4$  SOLUTION AFTER 20 HOURS

No	Compound	$\Delta\epsilon$	$\lambda_{\text{max}}$ nm	Predicted sign
17	5 $\alpha$ -cholest-1-ene	-0.10	440	-
18	5 $\alpha$ -cholest-2-ene	+0.022	440	-
19	5 $\alpha$ -cholest-3-ene	+0.08	440	+
20	cholest-4-ene	No detectable C.D.		
21	cholest-5-ene	No detectable C.D.		
22	5 $\alpha$ -cholest-7-ene	No detectable C.D.		
23	3 $\beta$ -acetoxy ergost-8(9)-en-5 $\alpha$ -ol	No detectable C.D.		
24	5 $\alpha$ , 25D-spirost-9-en-3 $\beta$ -ol	No detectable C.D.		
25	5 $\alpha$ , 25D-spirost-11-en-3 $\beta$ -ol	Weakly negative		
26	3 $\beta$ -hydroxy androst-16-ene	+0.09	440	+
27	3 $\beta$ -hydroxy-17-methylene androstane	+0.16	450	-
28	3 $\beta$ -hydroxy pregnane-20-ene	-0.104	425	?
29	3-methyl cholest-2-ene	-0.005	450	-
30	lanost-2-ene	-0.001	460	?
		+0.01	410	?
31	5 $\beta$ -cholest-3-ene	+0.002	430	+
32	cholesterol	No detectable C.D.		
33	6-methyl cholest-5-en-3 $\beta$ -ol	No detectable C.D.		
34	3-methylene cholestane	+0.012	440	?
35	3 $\beta$ -acetoxy-7-methylene cholestane	+0.05	440	?
36	3 $\beta$ -acetoxy-11-methylene-5 $\alpha$ , 25-spirostan	No detectable C.D.		
37	16 $\beta$ -methyl-3 $\beta$ , 11 $\beta$ , 20-triacetoxy-5 $\alpha$ -pregn-17(20)-ene	No detectable C.D.		
38	20, 20-ethylene dioxy-11 $\alpha$ -methyl-5 $\alpha$ -pregn-16-ene-3 $\beta$ , 11 $\beta$ -diol	No detectable C.D.		
39	iso-lanostene	No detectable C.D.		

The quadrant projections for a selection of olefins are given in Figs. 11-13 and are found generally to fit the derived rule assuming, not unreasonably, that attachment of the Pt occurs on the less hindered side of the double bond as determined from an inspection of molecular models.

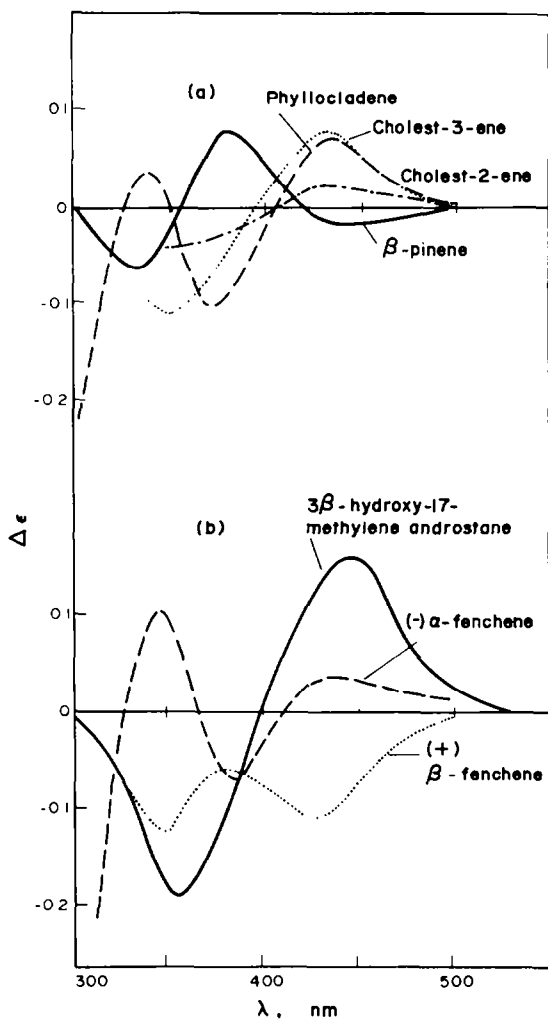


FIG 10. CD spectra of (a)  $(-)\beta$ -pinene ———, phyllocladene - - - - - ,  $5\alpha$ -cholest-2-ene — · — · — and  $5\alpha$ -cholest-3-ene · · · · · and (b)  $3\beta$ -hydroxy-17-methylene androstane ———,  $(-)\alpha$ -fenchene - - - - - and  $(+)\beta$ -fenchene · · · · · in alcoholic sodium tetrachloroplatinate.

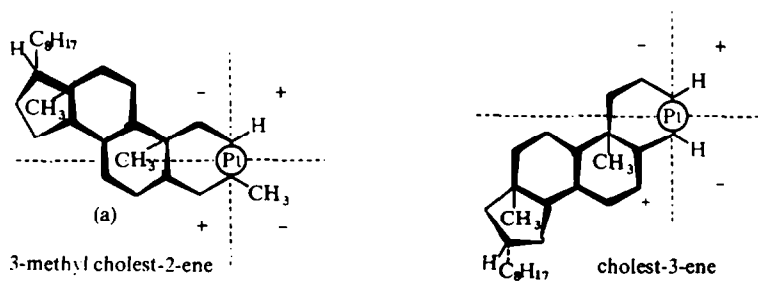


FIG 11. Quadrant projections for the Pt complexes of (a) 3-Me  $5\alpha$ -cholest-2-ene and (b)  $5\alpha$ -cholest-3-ene.

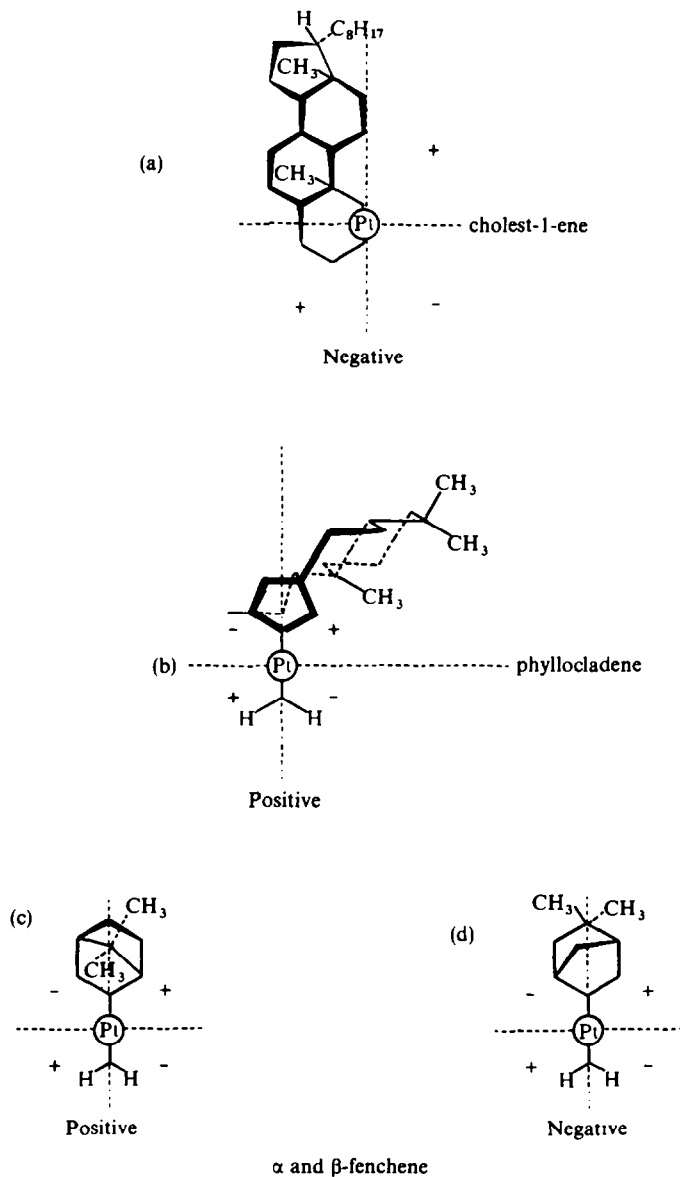


FIG 12. Quadrant projections for the Pt complexes of (a) 5 $\alpha$ -cholest-1-ene, (b) phyllocladene, (c) (-) $\alpha$ -fenchene and (d) (+) $\beta$ -fenchene.

However, a number of exceptions are noted. (-)  $\beta$ -Pinene (XI) is known to hydrogenated catalytically from the  $\alpha$  side of the double bond giving (-) *cis*-pinane<sup>39</sup> as would be expected from steric considerations. By analogy, it is assumed that complexation to Pt again involves the  $\alpha$  side of the double bond. The expected result from quadrant considerations (Fig. 13a) is a positive effect contrary to the observed negative effect for the long wavelength CD band (Fig. 10). As yet the origin of this

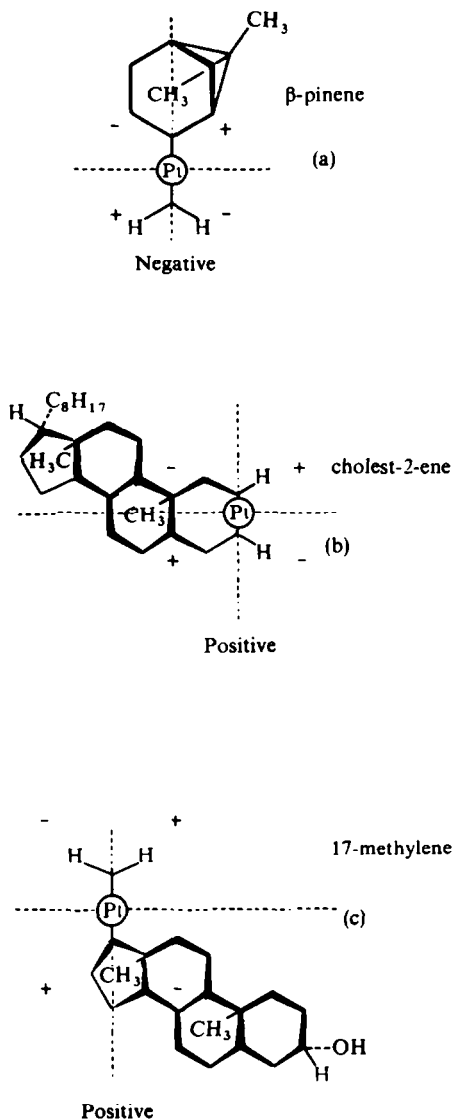
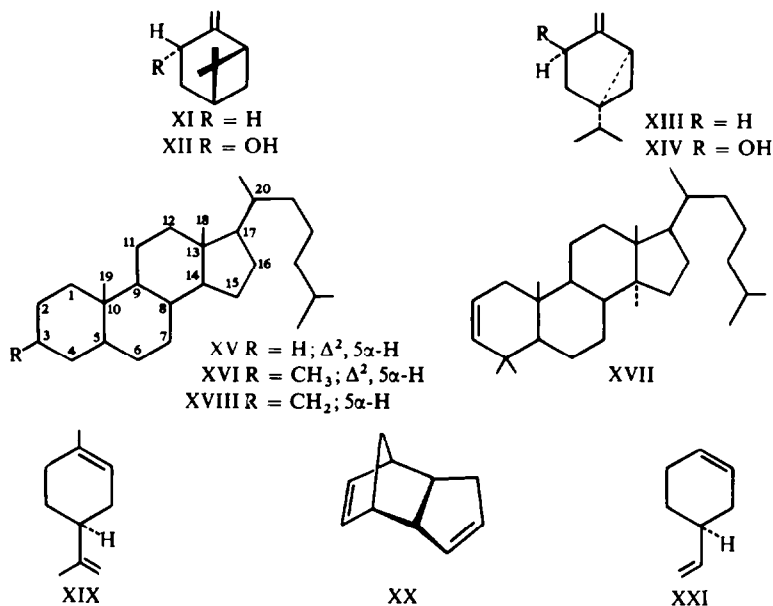


FIG 13. Quadrant projections for the Pt complexes of (a) (-)  $\beta$ -pinene, (b)  $5\alpha$ -cholest-2-ene and (c)  $3\beta$ -hydroxy-17-methylene androstane.

reversal is not fully understood, although it is thought that the unusual polarizability of the cyclobutane ring may be responsible.<sup>40</sup> In this context, however, it is noted that even the detailed application of the Octant Rule for ketones to bridged systems such as (+) camphor is not simple because there is as yet no quantitative knowledge of the dependence of the Cotton Effect on the distance of a substituent from the chromophore.<sup>41</sup>



(+)-*trans*-Pinocarveol (XII) possesses the same stereochemistry as (-)- $\beta$ -pinene (XI). However it exhibits an oppositely signed CD band (no. 6, Table 1). Perhaps the steric hindrance created by the  $\alpha$ -hydroxyl-function is responsible for the instability of the complex, as decomposition to platinum black occurs readily.

(+) Sabinene (XIII) has been shown to hydrogenate predominately from the side of the cyclopropane ring under controlled conditions.<sup>42</sup> Assuming complexation to occur from this side of the double bond, the observed negative long wavelength CD band implies a normal contribution from the cyclopropane ring. (+) Sabinol (XIV) in addition to exhibiting a negative CD band in the same region possesses a weaker positive band at longer wavelength. This can be attributed to some special effect from the weak coordination of the OH function to Pt.

5 $\alpha$ -Cholest-2-ene (XV) exhibits a weak positive effect (Fig. 10) opposite to that predicted from the quadrant rule, assuming attachment to the  $\alpha$  side of the double bond (Fig. 13b). The reason for this is again not fully understood but the anomaly may originate either from unsymmetrical coordination of the double bond to Pt<sup>43</sup> or (as seems more likely) from a change of sector sign contribution on moving further from the chromophore. Such a sign change could be envisaged as arising from the planes involving the  $d_{xy}$  and  $d_{z^2}$  orbitals of Pt.

With 5 $\alpha$ -3-methyl cholest-2-ene (XVI), the CD conforms to that predicted from the quadrant rule again assuming attachment from the  $\alpha$  side of the double bond (Fig. 11a). Lanost-2-ene (XVII) produces two very weak CD bands of alternating sign above 400 nm when complexed to Pt. It is probable that this results from the conformational mobility known to occur in ring A of 4,4-dimethyl substituted steroids.<sup>41</sup>

The result obtained with 3-methylene cholestane (XVIII) is that which would have been predicted for  $\beta$  attachment of the Pt to the double bond. Inspection of molecular models reveals that the  $\beta$  side may be somewhat less hindered than the  $\alpha$  side.

Contrary to expectation 3 $\beta$ -hydroxy-17-methylene androstane yielded a positive Cotton Effect on complexation (Fig. 13c). Since the  $\alpha$  side of the double bond is



certainly the less hindered the only possible explanation at present available is that the quadrants do indeed change sign further away from the chromophore as envisaged for  $5\alpha$ -cholest<sup>2</sup>-ene.

Such a generalised rule, effectively a double octant rule, would permit application of the above results to optically active chelating dienes such as limonene. These complexes can be obtained crystalline as Type III structures (see above). The ORD and CD curves for the complex derived from (–) limonene, XIX, viz. (+) *cis*-dichloro-(limonene) platinum II, are given in Fig. 14. Antipodal ORD and CD curves were obtained for the enantiomorph using (+) limonene. Owing to chelate formation the first wavelength CD transition occurs at higher energy in a position analogous to the *cis*-amine olefin complexes.<sup>2</sup>

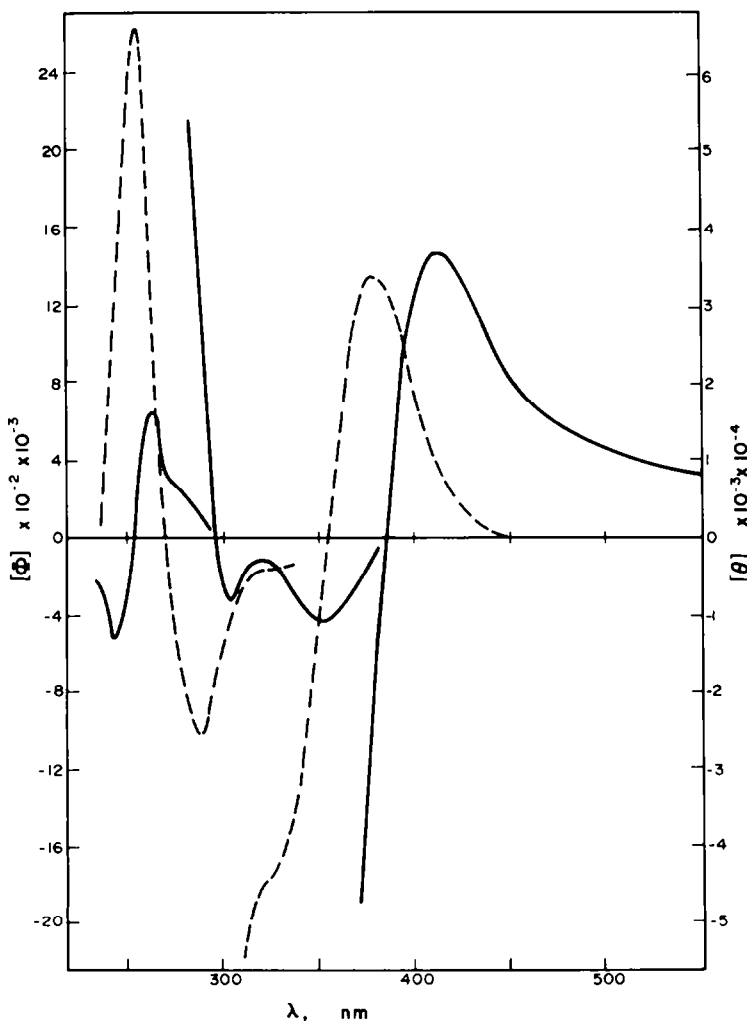
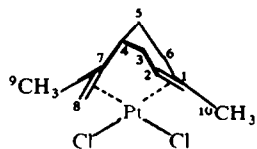


FIG 14. ORD ————— and CD - - - - - spectra of (+)*cis*-dichloro-((-)limonene) Pt II in  $\text{CH}_2\text{Cl}_2$ .

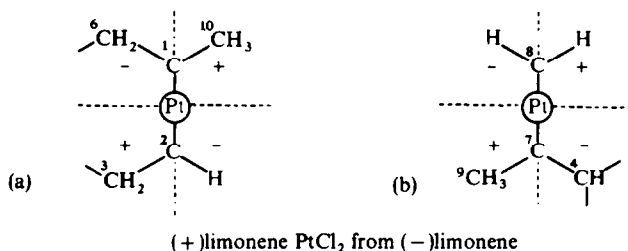
The X-ray analysis of dipentene platinum dichloride has revealed the chelate structure given in Fig. 15.<sup>22</sup>



X-ray of (-)-limonene PtCl<sub>2</sub> from (+)-limonene

FIG 15. Structure of dipentene platinum dichloride (X-ray analysis).<sup>22</sup> The structure represents that obtained from (+)-limonene i.e. (-)-*cis*-dichloro-[(+)-limonene] Pt II.

Application of the generalised rule is simplified for the complex derived from (-)-limonene by a consideration of each olefinic region separately (Fig. 16).



(+)-limonene PtCl<sub>2</sub> from (-)-limonene

FIG 16. Quadrant projections for (a) the 1,2 double bond and (b) the 7,8 double bond of the Pt complex from (-)-limonene.

Contributions from the quadrants created around the 7(8) double bond effectively cancel. At the 1(2) double bond the contribution is positive as observed for the long wavelength transition.

Recently, the resolution of *endo*-dicyclopentadiene (XX) through its Pt complex has been reported.<sup>44</sup> In order to provide a further example of the application of the method to a bidentate ligand the resolution was repeated and a sample of (-)-*endo*-dicyclopentadiene [ $\alpha$ ]<sub>D</sub>-14.1° obtained. The ORD and CD spectra of the derivatives (-)-*cis*-dichloro[(-)-*endo*-dicyclopentadiene] Pt(II) are shown in Fig. 17. Application of the quadrant rule to each double bond in turn predicts the absolute configuration XX. Since (-)-*cis*-dichloro[(-)-*endo*-dicyclopentadiene] Pt(II) can be converted with cyanide ion to (-)-*endo*-dicyclopentadiene the absolute configuration of the levo-rotatory enantiomer is as shown (XX).

Furthermore the olefin (XX) lends itself to octant rule analysis. Its ORD and CD data are illustrated in Fig. 18. The analysis leaves no doubt that the (-)-diene has the absolute configuration of XX and moreover the possible existence of exciton splitting which was used<sup>45</sup> to deduce the opposite configuration for (-)-*endo*-dicyclopentadiene† is not reflected in the observed CD spectrum which is normal in *position* and *intensity* for *cis*-disubstituted olefins i.e. a positive  $\pi_x \rightarrow \pi_x^*$  band at 202 nm followed by an oppositely signed high energy band ( $\sigma \rightarrow \pi^*$  or  $\pi_x \rightarrow \pi_y^*$ ) near 185 nm.<sup>1</sup>

† It appears that a sign reversal or misprint was responsible for this assignment, for alternating bands of the opposite sign to those shown were predicted by the coupled oscillator theory.

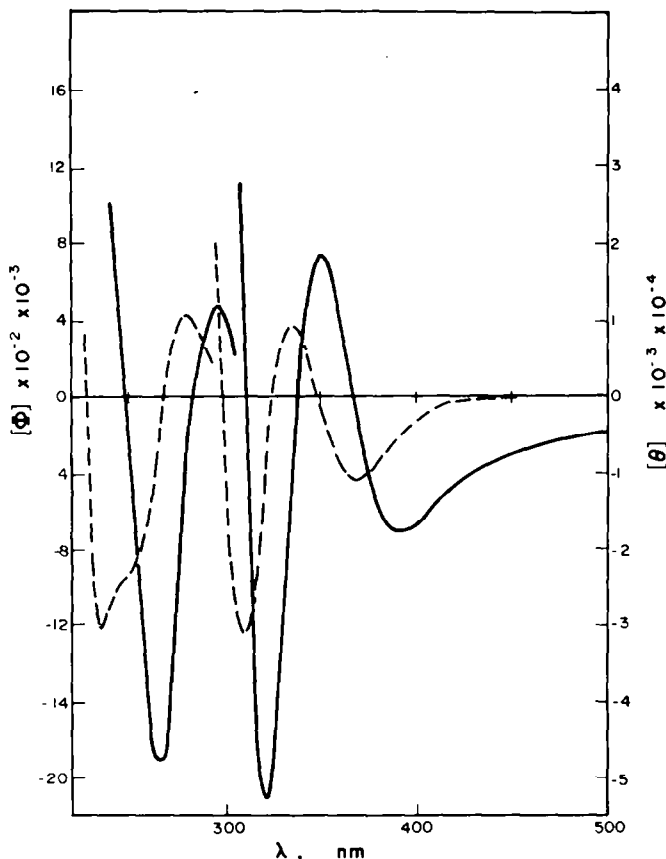


FIG 17. ORD ——— and CD - - - - - spectra of (-)-*cis*-dichloro [(-)-*endo*-dicyclopentadiene] Pt II in  $\text{CH}_2\text{Cl}_2$ .

It is worthy of note that both (-)-limonene (XIX) and (-)-*endo*-dicyclopentadiene (XX) possess the same sign of the olefin  $\pi \rightarrow \pi^*$  Cotton effect. However their Pt complexes display oppositely signed d-d transitions. This effect is attributed to the occupation of positive quadrants by the Me groups of (-)limonene in the complex, an effect for which the Pt(II) complex of (-)-*endo*-dicyclopentadiene has no alkyl counterpart (see Fig. 16). In this context it became of crucial interest to examine the chiroptical properties of 4-vinylcyclohexene (XXI) and its Pt(II) complex,<sup>13b</sup> where we would predict for that enantiomer with a negative  $\pi \rightarrow \pi^*$  CD the same absolute configuration as (-)limonene. However for this particular array the absence of Me quadrant occupancy should lead to a negative CD for the d-d Pt transition. The reverse situation would apply for the enantiomer with a positive  $\pi \rightarrow \pi^*$  CD. A sample of (+) 4R-vinyl cyclohexene† kindly provided by Professor J. A. Berson and Mr. P. Dervan was found to conform in every respect with this prediction i.e. the olefin exhibited a positive ORD *extremum* at 215 nm while the corresponding Pt(II) complex

† The absolute configuration has been defined by a rigorous chemical conversion (J. A. Berson and P. Dervan, *private communication*).

showed a *positive* Cotton Effect at 380 nm. The absolute configuration  $4R$  of (+) vinyl-cyclohexene is thereby confirmed (XXI shows the  $4S$  absolute configuration).

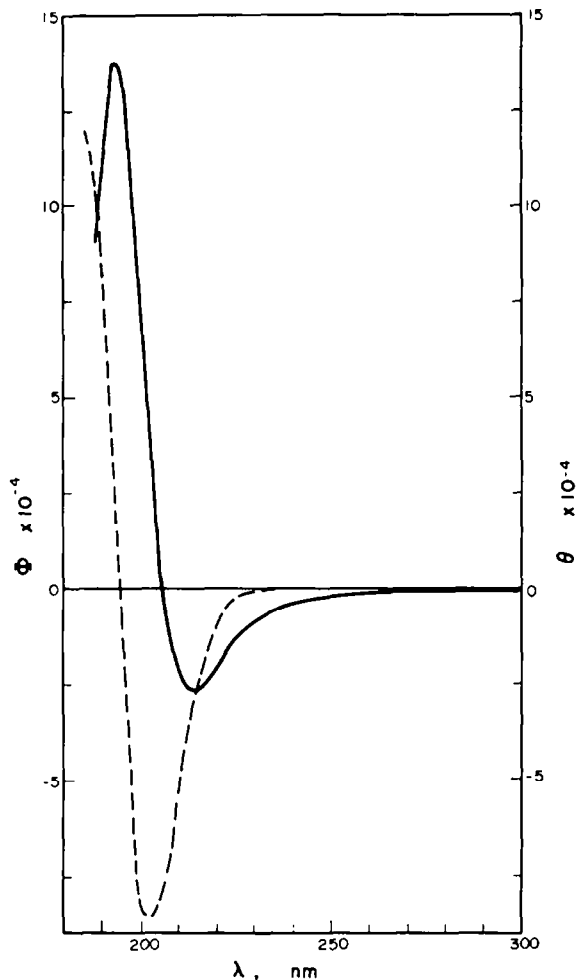


FIG 18. ORD ————— and CD - - - - - spectra of (-) *endo*-dicyclopentadiene in cyclohexane.

The quantitative recovery without *cis-trans* rearrangement of the olefin after complexation has been obtained with simpler olefins using cyanide.<sup>11, 46</sup> Each of the olefins used in the CD work was recovered, after use, with NaCN and analytical TLC or vapour phase chromatography was used to detect possible isomerisation or decomposition. Commonly, 10 to 30 mg of olefin were used for the CD measurement (by using longer path lengths, smaller quantities of olefin could be used) and recovery afterwards was normally of the order 80 to 90%.

Isomerization or racemisation was noted in a number of cases and was usually attributed to the quality of the sodium tetrachloroplatinate. At low pH the CD spectrum of (-)  $\beta$ -pinene in alcoholic sodium tetrachloro platinate solution increased

with time until a maximum was reached (at about 25 hr). Thereafter, the CD peak collapsed and  $\alpha$ -pinene and other products were detected on recovery with cyanide. A similar occurrence was noticed with (+) sabinene but not with (+) sabinol. In acidic tetrachloroplatinate, (–) limonene was found to give the racemic dipentene complex in MeOH, EtOH or n-PrOH as solvent.

With the olefin complexes resolved through the use of optically active  $\alpha$ -methylbenzylamine, in a number of cases mutarotation was found to occur in solution. This has already been noted for the *trans*-2-butene complexes<sup>27</sup> and is here found to occur for the *trans*-cyclononene, *trans*-cyclodecene and *trans*-bicyclo[8.2.2]tetradeca-5,10,12,13-tetraene complexes. The process presumably involves reversible dissociation of the olefin complexes, permitting the olefin to racemise while dissociated. The CD spectrum eventually obtained arises from the contribution of the optically active amine. Addition of a drop of the free olefin greatly hastened the mutarotation. In fact an NMR study<sup>47</sup> has previously shown rapid exchange between free and complexed ethylene, a similar observation being made here with the *trans*-cyclooctene complexes, which only mutarotated in the presence of uncomplexed olefin.

With sterically hindered olefinic double bonds a lower degree of complexation favours decomposition of the tetrachloroplatinate ion to Pt black, presumably through oxidation of the solvent. Such is the case with camphene, cholesterol etc. When complexation does occur, the solution normally changes colour from red to light yellow.

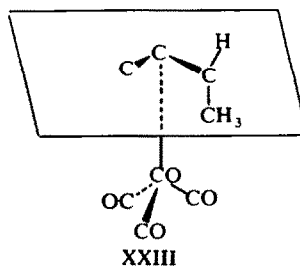
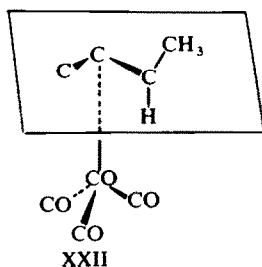
In this study little account has been taken of the possibility of rotation about the Pt-olefin axis.<sup>48</sup> Since such rotation does not produce a change in absolute configuration of the olefin carbon centres and since the situation where the olefin double bond lies in the Pt square plane is thought to be at higher energy,<sup>49</sup> it is probable that such rotation does not affect our arguments.

In summary, provided that care is taken over the purity of the sodium tetrachloroplatinate used, and if the olefin is recovered soon after CD measurement, the proposed rule may, under favourable circumstances, yield information relating to the absolute stereochemistry of a given optically active olefin with little loss of material after use.

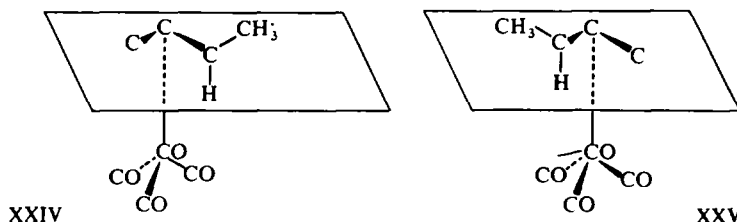
#### APPENDIX

##### *Optically Active $\pi$ -Allyl Palladium Complexes*

Unsymmetrically substituted allyl groups on coordination to a metal can exhibit both geometrical and optical isomerism. Thus the  $\pi$ -allyl complex  $C_4H_7 \cdot Co(CO)_3$  is formed as a mixture of geometrical isomers<sup>50</sup> (see XXII and XXIII).



The *syn* isomer (XXII) is in this case thermally the more stable, conversion of the *anti* isomer (XXIII) into the *syn* being permitted at 80°C.<sup>51</sup> Both geometrical isomers are dissymmetric, a centre of asymmetry being created at the substituted carbon atom on coordination.<sup>52</sup> Thus for the *syn* isomer the optical antipodes are demonstrated by XXIV and XXV. Resolution in a similar manner to the  $\pi$ -olefin complexes of Pt<sup>27</sup>



is possible and has been achieved with certain  $\pi$ -allyl complexes of Pd using optically active  $\alpha$ -methyl benzylamine.<sup>52</sup> Thus chloro-(1-acetyl-2-methyl- $\pi$ -allyl)-(S)-( $\alpha$ -methyl benzylamine) Pd(II) on crystallisation yields the negatively rotating diastereoisomer<sup>52</sup> through a second order asymmetric transformation similar to that observed with the *trans*-2-butene Pt complexes.<sup>27</sup> Only at low temperatures is the rotation strongly negative and at room temperature epimerisation rapidly occurs yielding an equilibrium rotation which is probably due to the coordinated amine.<sup>52</sup>

Through the use of optically active  $\pi$ -allyl ligands it should be possible to stabilise one of the enantiomorphic forms owing to steric requirements, in much the same way as with Pt-olefin complexes. Thus with steroidal derivatives complexation would be expected to take place preferentially in one direction.

Recently<sup>53, 54</sup> some  $\pi$ -allyl steroidal derivatives of Pd have been prepared and an initial ORD and CD study of these complexes was undertaken in order to examine their possible use as chromophoric derivatives in cases where the method with platinum-olefin complexes failed. Unlike the platinum-olefin complexes,  $\pi$ -allyl derivatives of Pd could usually be isolated in the crystalline state and were generally much more stable and soluble in organic solvents. Not only could such complexes be obtained from olefins<sup>16, 55</sup> but also from dienes<sup>56</sup> and enones.<sup>57</sup>

## RESULTS AND DISCUSSION

The results for a number of  $\pi$ -allyl complexes derived from cholest-4-en-3-one and analogous steroidal enones are given in Table 4, and representative ORD and CD curves are reproduced in Fig. 19.

TABLE 4. C.D. SPECTRA (LONG WAVELENGTH BAND) OF 3-OXO- $\Delta^4$ -5-STEROIDAL Pd II-ALLYL DERIVATIVES IN CH<sub>2</sub>Cl<sub>2</sub> SOLUTION

No	Compound	$[\theta]$	$\lambda_{\max}$ nm
1	cholest-4-en-3-one-PdCl	+ 17,100	393
2	cholest-4-en-3-one-PdI	+ 18,290	413
3	cholest-4-en-3-one-PdClpy <sup>a</sup>	+ 22,140	379
4	progesterone-PdCl	+ 20,850	393
5	androst-4-en-3,17-dione-PdCl	+ 21,000	393
6	3-oxo-androst-4,17-diene-PdCl	+ 25,300	393

<sup>a</sup> Exists as a monomer while the others are partly dimerised in solution.

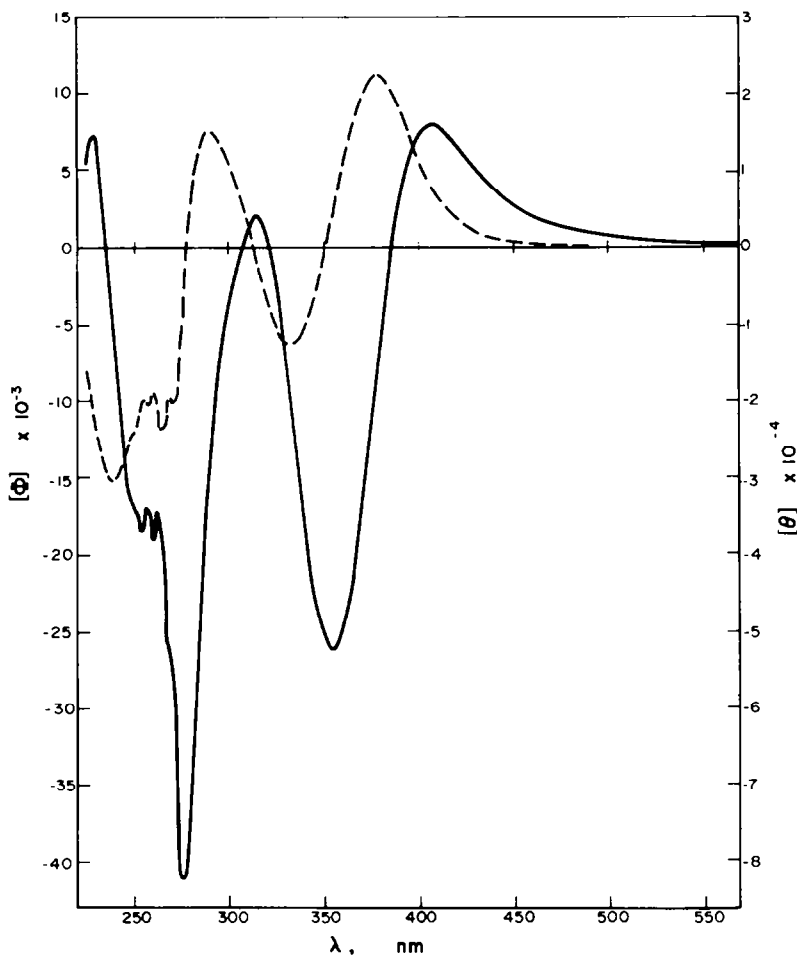


FIG 19. ORD ————— and CD - - - - - spectra of cholest-4-en-3-one-PdClpy in  $\text{CH}_2\text{Cl}_2$ .

Since for our purposes the method would prove valuable only with isolated olefinic double bonds, attempts were made to prepare  $\pi$ -allyl derivatives from compounds containing only olefinic double bonds as functional groups. Thus androst-5-ene yielded a  $\pi$ -allyl complex which exhibited the ORD and CD spectra given in Fig. 20. A similar complex was obtained from (–)  $\beta$ -pinene and its spectra are given in Fig. 21.

Although the preparation of the  $\pi$ -allyl complex from (–)  $\beta$ -pinene yielded only one such complex, when  $\alpha$ -pinene was used two complexes could be obtained (Table 5). These could be separated by repeated TLC the one in smaller amount being found identical to that derived from (–)  $\beta$ -pinene. In fact (–)  $\alpha$ -pinene yielded the complex with the same sense of rotation as that obtained from (–)  $\beta$ -pinene, confirming the previous correlations through the same hydrogenation product (–) *cis*-pinane<sup>39</sup> or through the isomerisation of  $\beta$ -pinene with the same sense of rotation.<sup>58</sup>

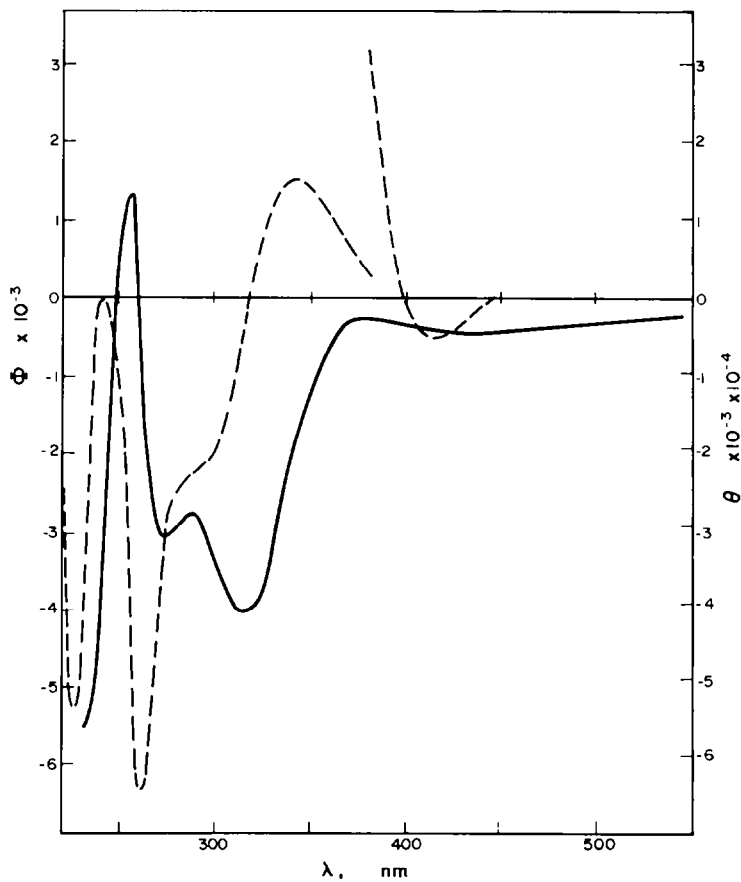


FIG 20. ORD ----- and CD ----- spectra of androst-5-ene-PdCl in  $\text{CH}_2\text{Cl}_2$ .

TABLE 5. CD SPECTRA OF Pd CHLORIDE II-ALLYL DERIVATIVES OF MONOTERPENE AND STEROID OLEFINS

No	Compound	Long wavelength band		Lower band	
		$[\theta]$	$\lambda_{\text{max}}$ nm	$[\theta]$	$\lambda_{\text{max}}$ nm
7	(-) $\beta$ -pinene	-68	421	+2,425	345
8	(-) $\alpha$ -pinene	-	420	+	345
	top spot on t.l.c.	-	360	+	310
9	androst-5-ene	-50	415	+1,530	344
10	cholest-4-ene	-290	408	+1,800	340
	top spot on t.l.c.	+	378	-	340
11	3-methyl cholest-2-ene	-	-	-3,620	340
	top spot <sup>a</sup> on t.l.c.	+130	405	-790	338

<sup>a</sup> Apparently the stronger lower lying band at 340 nm here conceals the weaker transition of opposite sign at about 400 nm.



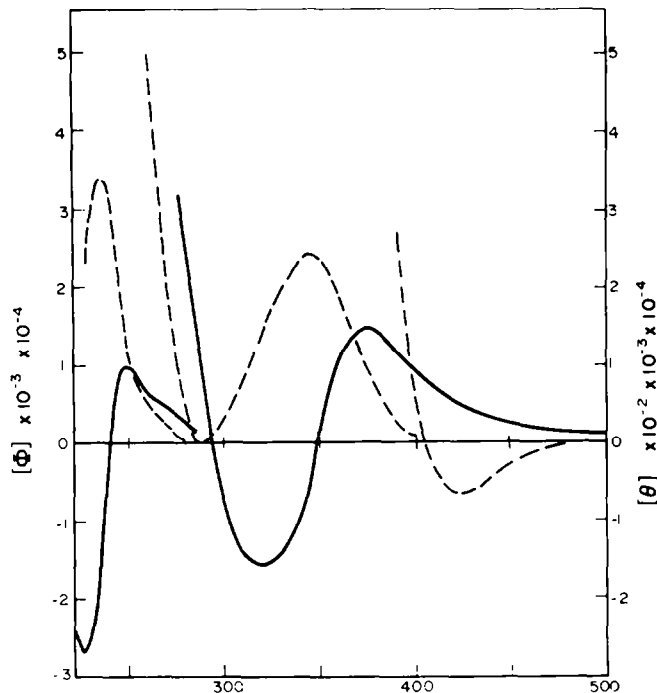


FIG 21. ORD ————— and CD - - - - - spectra of  $\beta$ -pinene-PdCl in  $\text{CH}_2\text{Cl}_2$ .

### CONCLUSION

Although Pd  $\pi$ -allyl complexes possess the advantage of greater stability and are more readily isolated and purified, the yields are often relatively small, a large proportion of unreacted olefin being recovered after reaction. In the case of *cis*- and *trans*-cyclooctene no  $\pi$ -allyl complexes could be obtained, on the  $\pi$ -olefin complexes being formed.

With enones, the conjugated unsaturated ketone can be recovered after measurement using  $\text{SnCl}_2$  in MeOH followed by reduction.<sup>53</sup> However with olefins, recovery would be expected to lead to a mixture of products. For these reasons and the fact that a given olefin may produce a number of  $\pi$ -allyl complexes which would require separation before spectral measurement, the method is thought to be of less value than using Pt olefin complexes. Even so, it is noted that with olefins such as androst-5-ene the method yields a measurable CD spectrum whereas the complexes with Pt exhibit no detectable CD. In addition the method is seen to possess some application to unsaturated ketones.

### EXPERIMENTAL

ORD and CD curves were measured at 25° with a JASCO ORD/UV-5 or a Cary Model 60 spectropolarimeter equipped with a 6001 CD accessory. Path lengths of 50, 10 or 1 mm were used. Unless otherwise stated all measurements were made in spectra grade  $\text{CH}_2\text{Cl}_2$ .

### Olefins

The authors gratefully acknowledge a gift of several steroidal olefins from Professor G. D. Meakins<sup>59</sup> and several monoterpene olefins from Dr. A. F. Thomas of Firmenich and Cie, Geneva. The diterpene olefins were kindly supplied by Professor R. C. Cambie. (+) and (-)  $\alpha$ -pinene were obtained from Aldrich Chem. Co. and (-)  $\beta$ -pinene and (+) and (-) limonene ("purum") from Fluka. The pinenes were purified either by vapour phase chromatography on Carbowax 20M (20 ft. column) or by preparative TLC on HF 254 silica impregnated with 10%  $\text{AgNO}_3$  using 0.5 mm thickness and 30%  $\text{C}_6\text{H}_6$  in petroleum ether as solvent. (+) and (-) limonene were used without further purification.

A mixture of (-)  $\alpha$ - and (+)  $\beta$ -fenchene prepared from fenchone, were separated by vapour phase chromatography on  $\text{AgNO}_2$ /ethylene glycol on 80–100 mesh chromosorb P (15 ft. column) at 65°C and 200 ml/min. He. Analytical vapour phase chromatography of the monoterpenes was carried out either on 20% PEG 5400 on 80–100 mesh chromosorb P (20 ft. column) at 45°C and 125 ml/min.  $\text{N}_2$  or on PEG 6000 (5 ft. column) at 100°C and 60 ml/min.  $\text{N}_2$ . Unless otherwise indicated, analytical TLC was carried out using either silica gel G and elution with 30% EtOAc/petroleum ether (60–80) or  $\text{AgNO}_3$  impregnated silica gel and elution with 30%  $\text{C}_6\text{H}_6$ /petroleum ether.

Endocyclic steroidal olefins were synthesised by standard literature methods and possessed physical constants in good agreement with those already recorded. Exocyclic methylene derivatives of steroids were formed by Wittig reactions on the corresponding ketone using the procedure of Sondheimer and Mechoulam.<sup>60</sup>

*trans*-Cyclooctene. Cyclooctylamine (100 g) (Aldrich) was converted to the dimethylamine by the known procedure<sup>61</sup> using 90%  $\text{HCOOH}$  (204 g) and 37%  $\text{HCHO}$  (180 ml). Conversion to the trimethylammonium hydroxide followed by pyrolysis under reduced pressure gave a mixture of *cis* and *trans* cyclooctene which was separated by taking advantage of the solubility of the *trans*-isomer in  $\text{AgNO}_3$  soln.<sup>62</sup> The olefins were distilled (reduced pressure) and analysed by VPC.<sup>62</sup>

### Pt Complexes

A gift of samples of the cycloolefin complexes of platinum from the late Professor A. C. Cope and Dr. B. A. Pawson is gratefully acknowledged.

*Resolution of  $\alpha$ -Me benzylamine.* The resolution of *dl*  $\alpha$ -Me benzylamine was achieved according to the reference procedure.<sup>63</sup> The (+) amine (b.p. 184–185°,  $[\alpha]_D + 40^\circ$  (neat)) was obtained through fractional crystallisation of the *l*-malate and the (-) amine (similar b.p. and rotation of opposite sense) through fractional crystallisation of the *d*-tartrate. ORD of (+) isomer in  $\text{CH}_2\text{Cl}_2$ :  $c$  2.676 (606–290 nm)  $[\Phi]_{600} + 35.8^\circ$ ;  $c$  0.1338 (290–225 nm)  $[\Phi]_{285} + 222^\circ$ ,  $[\Phi]_{271} + 54^\circ$ ,  $[\Phi]_{267} + 310^\circ$ ,  $[\Phi]_{264} + 220^\circ$ ,  $[\Phi]_{260} + 485^\circ$ ,  $[\Phi]_{257} + 533^\circ$ ,  $[\Phi]_{230} + 990^\circ$ ,  $[\Phi]_{225} + 711^\circ$ . CD of (+) isomer in  $\text{CH}_2\text{Cl}_2$ :  $c$  0.1338  $[\theta]_{275.0}$ ,  $[\theta]_{267.5}$  330,  $[\theta]_{265} - 205$ ,  $[\theta]_{262} - 400$ ,  $[\theta]_{258} - 290$ ,  $[\theta]_{256.5} - 320$ ,  $[\theta]_{230.0}$ ,  $[\theta]_{225} + 4,900$ .

*Zeise's Salt.* Potassium trichloro-(ethylene)-platinate II (Zeise's salt) was prepared by treatment of an acidified soln of potassium tetrachloroplatinate II with ethylene according to the procedure of Chatt and Searle.<sup>64</sup> This compound was used without further purification or converted into di- $\mu$ -chloro-1,3-dichloro-2,4-bis-(ethylene) di-Pt II which was purified by rapid recrystallisation from toluene.

*trans*-Dichloro-(ethylene)-( $\alpha$ -methyl benzylamine)-platinum II. Crude *trans*-dichloro-(ethylene)-( $\alpha$ -methyl benzylamine)-Pt II was precipitated from a cooled soln of KCl and Zeise's salt in dil HCl on addition of the appropriate molar quantity of resolved  $\alpha$ -methylene benzylamine and slowly basifying to pH 5.<sup>30</sup> Often the crude product was obtained as an oil and could be extracted with  $\text{CH}_2\text{Cl}_2$ . Attempts to purify this material further were unsuccessful and a purer sample for ORD and CD measurements was prepared by the addition of the correct quantity of amine to the bridged dimer in  $\text{CH}_2\text{Cl}_2$  soln. The purest sample had m.p. 60–70°,  $[\alpha]_D + 12^\circ$  for the complex prepared from (+)  $\alpha$ -methyl benzylamine. *trans*-Dichloro-(ethylene)-( $\alpha$ -methylamine)-platinum II<sup>30</sup> was prepared in a similar way from Zeise's salt and *d*-amphetamine. Purification by recrystallisation from cyclohexane or EtOAc, m.p. 120–121°,  $[\alpha]_D + 20^\circ$ .

(+) *trans*-Dichloro-(*trans*-cyclooctene)-(R)-( $\alpha$ -methylbenzylamine) Pt II. This compound was prepared from (+) *trans* dichloro-(ethylene)-(R) ( $\alpha$  methyl benzylamine) Pt (II) according to the procedure of Cope *et al.*<sup>30</sup> Fractional crystallisation from  $\text{CCl}_4$  (4 times) gave fine pale yellow needles m.p. and m.m.p. 133.5–135°,  $[\alpha]_D + 68^\circ$ . ORD in  $\text{CH}_2\text{Cl}_2$ :  $c$  0.130 (600–360 nm)  $[\Phi]_{600} + 345^\circ$ ,  $[\Phi]_{430} + 2170^\circ$ ,  $[\Phi]_{390.5}$ ,  $[\Phi]_{365} - 1970^\circ$ ;  $c$  0.013 (360–220 nm)  $[\Phi]_{328} 0^\circ$ ,  $[\Phi]_{258} + 16,890^\circ$ ,  $[\Phi]_{240} + 3650^\circ$ ,  $[\Phi]_{220} + 24,390^\circ$ . CD in  $\text{CH}_2\text{Cl}_2$ :  $c$ , 0.130 (450–360 nm)  $[\Phi]_{450} 0$ ,  $[\Phi]_{392} + 2580$ ,  $[\Phi]_{361} 0$ ;  $c$  0.013 (360–230 nm)  $[\Phi]_{298} - 3760$ ,  $[\Phi]_{270} - 1390$ ,  $[\Phi]_{269} - 1460$ ,  $[\Phi]_{266} 0$ ;  $[\Phi]_{248} + 13,500$ ,  $[\Phi]_{230} + 1450$ . The resolved diastereoisomers of *trans*-dichloro-(olefin)-(R)-( $\alpha$ -methyl benzylamine) Pt (II), in which the olefin was propy-

lene, styrene or *trans*-2-butene, were obtained in a similar manner to the above resolved complex in which the olefin was *trans*-cyclooctene.<sup>27b</sup> Owing to their rapid mutarotation in solution,<sup>27b</sup> no accurate spectral determination could be made.

(+) *trans*-Dichloro-(*trans*-cyclooctene)-(S)-(α-methyl benzylamine) platinum (II). This compound was prepared by the addition of (-) *trans*-cyclooctene to the appropriate quantity of *trans*-dichloro-(ethylene)-(S)-(α-methyl benzylamine) Pt (II) and recrystallisation from n-hexane m.p. 97–98°, [α]<sub>D</sub> - 25°. <sup>30</sup> ORD in CH<sub>2</sub>Cl<sub>2</sub>: c 0.238 (600–350 nm) [φ]<sub>600</sub> + 97°, [φ]<sub>422</sub> + 863°, [φ]<sub>398</sub> 0°, [φ]<sub>360</sub> - 1530°; c 0.0238 (350–225 nm) [φ]<sub>315</sub> - 460°, [φ]<sub>305</sub> - 960°, [φ]<sub>294</sub> 0°, [φ]<sub>260</sub> + 8250°, [φ]<sub>244</sub> 0°, [φ]<sub>238</sub> - 1280°, [φ]<sub>234</sub> 0°, [φ]<sub>225</sub> + 7800°. CD in CH<sub>2</sub>Cl<sub>2</sub>: c, 0.151 (450–350 nm) [φ]<sub>450</sub> 0°, [φ]<sub>392</sub> + 1320, [φ]<sub>360</sub> 0°; c 0.0151 (350–270 nm) [φ]<sub>295</sub> - 2020, [φ]<sub>270</sub> - 1170.

Di-μ-chloro-1,3-dichloro-2,4-bis-(*trans*-cyclooctene)-diplatinum II. Addition of excess *trans*-cyclooctene to sodium tetrachloroplatinate in EtOH gave an almost immediate precipitate of yellow *trans*-dichloro-bis-(*trans*-cyclooctene) platinum (II).<sup>5,13b</sup> In air the substance slowly lost *trans*-cyclooctene and at 120°C the loss was rapid and complete at 131°C giving an orange product which decomposed without melting at 190°C. From analysis and by comparison with the known *cis*-cyclooctene complexes,<sup>13b</sup> the orange product is thought to be di-μ-chloro 1,3 dichloro-2,4-bis-(*trans*-cyclooctene)-diplatinum (II) Bridge-splitting with α-methyl benzylamine gave racemic *trans*-dichloro-(*trans*-cyclooctene)-(α-methyl benzylamine) platinum (II).<sup>65</sup>

Using (-) *trans*-cyclooctene, (+) di-μ-chloro-1,3-dichloro-2,4-bis-(*trans*-cyclooctene)-diplatinum (II) was obtained [α]<sub>D</sub> + 158° (c 0.1125 CH<sub>2</sub>Cl<sub>2</sub>). ORD in CH<sub>2</sub>Cl<sub>2</sub>: c, 0.043 [φ]<sub>600</sub> + 553°, [φ]<sub>468</sub> + 2310°, [φ]<sub>436</sub> 0°, [φ]<sub>402</sub> - 2380°, [φ]<sub>355</sub> 0°, [φ]<sub>318</sub> + 2450°, [φ]<sub>310</sub> + 2240°, [φ]<sub>258</sub> + 14,000°, [φ]<sub>246</sub> 0°, [φ]<sub>240</sub> - 3150° [φ]<sub>232</sub> 0°, [φ]<sub>225</sub> + 8400°.

(-) *trans*-Dichloro-(*trans*-bicyclo [8,2,2] tetradeca-5, 10, 12, 13-tetraene)-(R)-(α-methyl benzylamine) platinum (II). ORD in CH<sub>2</sub>Cl<sub>2</sub>: c 0.1598 (600–340 nm) [φ]<sub>600</sub> - 160°, [φ]<sub>430</sub> - 1950°, [φ]<sub>410</sub> 0°, [φ]<sub>374</sub> + 5040°, c 0.016 (340–220 nm) [φ]<sub>315</sub> + 518°, [φ]<sub>285</sub> + 6740°, [φ]<sub>271</sub> + 415°, [φ]<sub>267</sub> + 2320°, [φ]<sub>265</sub> + 1970°, [φ]<sub>260</sub> + 3110°, [φ]<sub>253</sub> + 310°, [φ]<sub>238</sub> + 22 800°, [φ]<sub>224</sub> 0°. CD in CH<sub>2</sub>Cl<sub>2</sub> c 0.1598 (500–340 nm) [φ]<sub>480</sub> 0, [φ]<sub>405</sub> - 4820, [φ]<sub>370</sub> 0; c 0.016 (340–225 nm) [φ]<sub>330</sub> + 2390, [φ]<sub>300</sub> + 460, [φ]<sub>279</sub> + 4630, [θ]<sub>277</sub> + 4360, [θ]<sub>270</sub> + 3870, [θ]<sub>268</sub> + 3460, [θ]<sub>365</sub> + 3840, [θ]<sub>263</sub> + 3590, [θ]<sub>256</sub> + 4590, [θ]<sub>244</sub> + 1080, [θ]<sub>225</sub> + 56,600. The positively rotating complex with (S)-α-methyl benzylamine gave essentially antipodal ORD and CD spectra.

(+) *cis*-Dichloro-(limonene) platinum II. The complex was prepared according to the procedure of Chatt and Wilkins<sup>13a</sup> using (-) limonene and sodium tetrachloroplatinate. Recrystallisation from EtOAc gave pale yellow needles which decomposed above 170°, melting at 192°. ORD in CH<sub>2</sub>Cl<sub>2</sub>: c 0.134 (600–340 nm) [φ]<sub>600</sub> + 243°, [φ]<sub>410</sub> + 1450°, [φ]<sub>384</sub> 0°, [φ]<sub>352</sub> - 4320°; c 0.0134 (340–320 nm) [φ]<sub>320</sub> - 1630°, [φ]<sub>304</sub> - 3260°, [φ]<sub>294</sub> 0°, [φ]<sub>262</sub> + 64000°, [φ]<sub>252</sub> 0°, [φ]<sub>242</sub> - 54000°, [φ]<sub>230</sub> - 27 000°. CD in CH<sub>2</sub>Cl<sub>2</sub>: c 0.134 (450–340 nm) [θ]<sub>450</sub> 0, [θ]<sub>376</sub> + 3350, [θ]<sub>354</sub> 0; c 0.0134 (340–230 nm) [θ]<sub>290</sub> - 25 650, [θ]<sub>270</sub> 0, [θ]<sub>253</sub> + 65 600, [θ]<sub>236</sub> 0. (+) Limonene gave a complex with essentially antipodal ORD and CD values.

#### General procedure for platinum-olefin complexes

After filtration to remove suspended platinum sodium tetrachloroplatinate (approx. 0.0025M) in MeOH (5 ml) was added to a slight molar excess of the olefin. If necessary sufficient CH<sub>2</sub>Cl<sub>2</sub> was added to produce a homogeneous soln. CD measurements were routinely taken after 20 hr and complexation was generally shown by a change in soln colour from red to yellow with a corresponding change in the UV spectrum. If complexation did not occur, decomposition to Pt black was usually noted.

*General procedure for recovery of olefinic material.* Recovery of the olefin was achieved by shaking the solution containing the complex with cold NaCN aq. and extracting with CH<sub>2</sub>Cl<sub>2</sub>. For example, 5α-cholest-1-ene (6.3 mg) was recovered after the complexation of the olefin (8.9 mg) with Pt. The purity of the recovered olefin was checked by analytical vapour phase chromatography or TLC.

(-) *cis*-Dichloro(endo-dicyclopentadiene) platinum II. *cis*-Dichloro(endo-dicyclopentadiene) Pt II was prepared according to the method of Chatt *et al.*<sup>12b</sup> Conversion to di-μ-chloro-bis-(3a → 4,7,7a-tetrahydro-exo-methoxy-4,7-methanoindene-endo-5σ,2π) diplatinum II followed by bridge splitting with (+) R-α-Me benzylamine and fractional crystallisation from CCl<sub>4</sub> and cyclohexane yielded (+) chloro (3a,4,7,7a-tetrahydro-exo-6-methoxy-endo-4,7-methanoindene-endo-5σ,2π) (R-α-methyl benzylamine)-platinum (II) [α]<sub>D</sub> + 112° m.p. 73–81°. Reflux for 3 hr in 5N HCl and recrystallisation from CHCl<sub>3</sub>-ether afforded (-) *cis*-dichloro (endo-dicyclopentadiene) Pt (II).<sup>44</sup> ORD in CH<sub>2</sub>Cl<sub>2</sub>: c 0.1809 (600–250 nm) [φ]<sub>600</sub> - 108°, [φ]<sub>391</sub> - 713°, [φ]<sub>367.5</sub> 0°, [φ]<sub>351</sub> + 732°, [φ]<sub>338.5</sub> 0°, [φ]<sub>321</sub> - 2110°, [φ]<sub>311</sub> 0°, [ψ]<sub>296.5</sub>

+ 4670°.  $[\phi]_{283.5} 0^\circ$ ,  $[\phi]_{265} - 19100^\circ$ , c 0.03618. (250–225 nm)  $[\phi]_{248} 0^\circ$ ,  $[\phi]_{225} + 62000^\circ$ . CD in  $\text{CH}_2\text{Cl}_2$ : c, 0.1809 (460–260 nm)  $[\theta]_{460} 0$ ,  $[\theta]_{368.5} - 1090$ ,  $[\theta]_{348.5} 0$ ,  $[\theta]_{334.5} + 910$ ,  $[\theta]_{325} 0$ ;  $[\theta]_{309.5} - 3120$ ,  $[\theta]_{298} 0$ ,  $[\theta]_{278} + 10,520$ ,  $[\theta]_{268} 0$ , c 0.03618 (260–227 nm)  $[\theta]_{235} - 30,600$ ,  $[\theta]_{227} 0$ .

(-) *endo-dicyclopentadiene* was obtained from (-) *cis* dichlorotendodicyclopentadiene Pt (II) by shaking with NaCNaq and extracting with pentane according to the published procedure.<sup>44</sup> ORD in cyclohexene: c, 0.03215 (300–185 nm)  $[\phi]_{300} - 476^\circ$ ,  $[\phi]_{214} - 26,050^\circ$ ,  $[\phi]_{206} 0^\circ$ ,  $[\phi]_{193} + 138,500^\circ$ ,  $[\phi]_{185} + 54,600^\circ$ . CD in cyclohexane: c, 0.03215 (250–185 nm)  $[\theta]_{250} 0$ ,  $[\theta]_{202} - 86,7000$ ,  $[\theta]_{194} 0$ ,  $[\theta]_{185} + 119,000$ .

(+) 4-Vinyl cyclohexene. A gift of (+) 4-vinyl cyclohexene of low optical purity ( $[\alpha]_D + 2.56^\circ$ , c 22.18  $\text{CCl}_4$ ) from Professor J. A. Berson and Mr. P. Dervan is gratefully acknowledged. This compound exhibited a positive olefin Cotton Effect (positive extremum  $[\phi]_{215} + 91.3^\circ$ , (c, 0.3548 cyclohexene)) demonstrating the 4*R* absolute configuration.

(+) *cis*-Dichloro-(4-vinyl cyclohexene) platinum(II) was prepared according to Kuljian and Frye.<sup>13b</sup> Repetition of the procedure with (+) 4-vinyl cyclohexene (140 mg) yielded large yellow crystals of (+) *cis*-dichloro-(4-vinyl cyclohexene) Pt(II) (140 mg) after standing for 72 hr at room temperature. ORD in  $\text{CH}_2\text{Cl}_2$ : c 2.756  $[\phi]_{405} + 13.0^\circ$ ,  $[\phi]_{380} 0^\circ$ ;  $[\phi]_{360} - 21.7^\circ$ . CD in  $\text{CH}_2\text{Cl}_2$ : c, 2.756  $[\theta]_{450} 0$ ,  $[\theta]_{380} + 21.7$ ,  $[\theta]_{363} 0$ ,  $[\theta]_{340} - 43.4$ .

#### *$\pi$ -Allyl complexes of palladium*

A gift of the oxo-steroid  $\pi$ -allyl derivatives<sup>53</sup> and the  $\beta$ -pinene  $\pi$ -allyl complex of palladium from Dr. F. J. McQuillan is gratefully acknowledged.

*Cholest-4-en-3-one*-PdCl. ORD in  $\text{CH}_2\text{Cl}_2$ , c 0.18 (600–370 nm)  $[\phi]_{600} + 738^\circ$ ,  $[\phi]_{420} + 6510^\circ$ ,  $[\phi]_{396} 0^\circ$ , c 0.018 (370–225 nm)  $[\phi]_{365} - 13,280^\circ$ ,  $[\phi]_{334} 0^\circ$ ,  $[\phi]_{297} + 17,410^\circ$ ,  $[\phi]_{285} 0^\circ$ ,  $[\phi]_{267.5} - 26,900^\circ$ ,  $[\phi]_{246} - 17,480^\circ$ ,  $[\phi]_{232} - 22,600^\circ$ ,  $[\phi]_{225} - 21,100^\circ$ . CD in  $\text{CH}_2\text{Cl}_2$ , c 0.18 (500–360 nm)  $[\theta]_{500} 0$ ,  $[\theta]_{393} + 17,100$ ,  $[\theta]_{362} 0$ , c 0.018 (360–230 nm)  $[\theta]_{337} - 11,700$ ,  $[\theta]_{306} 0$ ,  $[\theta]_{281} + 33,300$ ,  $[\theta]_{260} 0$ ,  $[\theta]_{250} - 8170$ ,  $[\theta]_{238} - 1200$ ,  $[\theta]_{230} - 20,000$ .

*Cholest-4-en-3-one*-PdI. ORD in  $\text{CH}_2\text{Cl}_2$ , c 0.128 (600–380 nm)  $[\phi]_{600} + 2240^\circ$ ,  $[\phi]_{455} + 8920^\circ$ ,  $[\phi]_{416} 0^\circ$ ,  $[\phi]_{387} - 10,800^\circ$ , c 0.0128 (380–235 nm)  $[\phi]_{365.5} 0^\circ$ ,  $[\phi]_{340} + 9760^\circ$ ,  $[\phi]_{318} 0^\circ$ ,  $[\phi]_{260} - 55,250^\circ$ ,  $[\phi]_{235} - 39,850^\circ$ . CD in  $\text{CH}_2\text{Cl}_2$ , c 0.128 (560–370 nm)  $[\theta]_{560} 0$ ,  $[\theta]_{413} + 18,290$ ,  $[\theta]_{372} 0$  (370–235 nm)  $[\theta]_{367} - 670$ ,  $[\theta]_{362} 0$ ,  $[\theta]_{310} + 43,300$ ,  $[\theta]_{260} 0$ ,  $[\theta]_{235} - 40,300$ .

*Cholest-4-en-3-one* PdClpy. ORD in  $\text{CH}_2\text{Cl}_2$ : c 0.084 (600–350 nm)  $[\phi]_{600} + 108^\circ$ ,  $[\phi]_{406} + 7880^\circ$ ,  $[\phi]_{385} 0^\circ$ ,  $[\phi]_{353} - 26,180^\circ$ , c 0.0084 (350–225 nm)  $[\phi]_{321} 0^\circ$ ,  $[\phi]_{314} + 2160^\circ$ ,  $[\phi]_{306} 0^\circ$ ,  $[\phi]_{275} - 41,100^\circ$ ,  $[\phi]_{262} - 17,230^\circ$ ,  $[\phi]_{259} - 19,180^\circ$ ,  $[\phi]_{255} - 17,030^\circ$ ,  $[\phi]_{253} - 18,670^\circ$ ,  $[\phi]_{235} 0^\circ$ ,  $[\phi]_{228} + 7188^\circ$ ,  $[\phi]_{225} + 5890^\circ$ . CD in  $\text{CH}_2\text{Cl}_2$ , c 0.084 (500–350 nm)  $[\theta]_{500} 0$ ,  $[\theta]_{379} + 22,140$ ,  $[\theta]_{351.5} 0$ , c 0.0084 (350–225 nm)  $[\theta]_{333} - 12,730$ ,  $[\theta]_{313} 0$ ,  $[\theta]_{289} + 15,280$ ,  $[\theta]_{277.5} 0$ ,  $[\theta]_{270} - 20,600$ ,  $[\theta]_{268} - 19,610$ ,  $[\theta]_{264} - 24,230$ ,  $[\theta]_{260} - 18,870$ ,  $[\theta]_{257} - 20,750$ ,  $[\theta]_{255} - 19,920$ ,  $[\theta]_{239} - 30,740$ ,  $[\theta]_{225} - 15,280$ .

*Androst-4-en-3, 17-dione*-PdCl. ORD in  $\text{CH}_2\text{Cl}_2$ , c 0.067 (600–370 nm)  $[\phi]_{600} + 962^\circ$ ,  $[\phi]_{423} + 10,450^\circ$ ,  $[\phi]_{396} 0^\circ$ , c 0.0067 (370–225 nm)  $[\phi]_{366} - 18,300^\circ$ ,  $[\phi]_{337.5} 0^\circ$ ,  $[\phi]_{300} + 26,600^\circ$ ,  $[\phi]_{283} 0^\circ$ ,  $[\phi]_{265} - 30,650^\circ$ ,  $[\phi]_{243} - 17,500^\circ$ ,  $[\phi]_{225} - 21,550^\circ$ . CD in  $\text{CH}_2\text{Cl}_2$ : c 0.067 (500–360 nm)  $[\theta]_{500} 0$ ,  $[\theta]_{393} + 21,000$ ,  $[\theta]_{361} 0$ , c 0.0067 (360–225 nm)  $[\theta]_{338} - 12,000$ ,  $[\theta]_{313} 0$ ,  $[\theta]_{283} + 53,310$ ,  $[\theta]_{256} 0$ ,  $[\theta]_{248} - 3720$ ,  $[\theta]_{240} - 2420$ ,  $[\theta]_{225} - 11,800$ .

*Progesterone*-PdCl. ORD in  $\text{CH}_2\text{Cl}_2$ , c 0.188 (600–370 nm)  $[\phi]_{600} + 1275^\circ$ ,  $[\phi]_{420} + 10,090^\circ$ ,  $[\phi]_{396} 0^\circ$ , c 0.0188 (370–220 nm)  $[\phi]_{366} - 19,400^\circ$ ,  $[\phi]_{337.5} 0^\circ$ ,  $[\phi]_{300} + 26,600^\circ$ ,  $[\phi]_{284.5} 0^\circ$ ,  $[\phi]_{265} - 43,500^\circ$ ,  $[\phi]_{243} - 27,230^\circ$ ,  $[\phi]_{220} - 36,250^\circ$ . CD in  $\text{CH}_2\text{Cl}_2$ : c, 0.188 (500–350 nm)  $[\theta]_{500} 0$ ,  $[\theta]_{393} + 20,850$ ,  $[\theta]_{361.5} 0$ , c 0.0188 (350–225 nm)  $[\theta]_{337} - 12,600$ ,  $[\theta]_{313} 0$ ,  $[\theta]_{283} + 51,200$ ,  $[\theta]_{255} 0$ ,  $[\theta]_{248} - 2500$ ,  $[\theta]_{240} 0$ ,  $[\theta]_{225} - 8460$ .

3-Oxo-androst-4, 17-diene-PdCl. ORD in  $\text{CH}_2\text{Cl}_2$ , c 0.126 (600–340 nm)  $[\phi]_{600} + 1416^\circ$ ,  $[\phi]_{422} + 12,140^\circ$ ,  $[\phi]_{396} 0^\circ$ ,  $[\phi]_{366} - 23,450^\circ$ , c 0.0126 (340–225 nm)  $[\phi]_{335.5} 0^\circ$ ,  $[\phi]_{295} + 40,050^\circ$ ,  $[\phi]_{282} 0^\circ$ ,  $[\phi]_{264} - 61,800^\circ$ ,  $[\phi]_{240} - 35,750^\circ$ ,  $[\phi]_{225} - 45,350^\circ$ . CD in  $\text{CH}_2\text{Cl}_2$ , c 0.0252  $[\theta]_{500} 0$ ,  $[\theta]_{393} + 25,300$ ,  $[\theta]_{361.5} 0$ ,  $[\theta]_{338} - 15,100$ ,  $[\theta]_{308} 0$ ,  $[\theta]_{280} + 67,000$ ,  $[\theta]_{253} 0$ ,  $[\theta]_{245} - 4400$ ,  $[\theta]_{233} 0$ ,  $[\theta]_{225} + 3,550$ .

$\beta$ -Pinene-PdCl. ORD in  $\text{CH}_2\text{Cl}_2$ , c 0.25 (600–360 nm)  $[\phi]_{600} + 44.3^\circ$ ,  $[\phi]_{375} + 1470^\circ$ , c 0.025 (360–220 nm)  $[\phi]_{348} 0^\circ$ ,  $[\phi]_{320} + 1572^\circ$ ,  $[\phi]_{295} 0^\circ$ ,  $[\phi]_{250} + 9970^\circ$ ,  $[\phi]_{240} 0^\circ$ ,  $[\phi]_{225} - 26,800^\circ$ ,  $[\phi]_{220} - 23,800^\circ$ . CD in  $\text{CH}_2\text{Cl}_2$ , c 0.25 (480–360 nm)  $[\theta]_{480} 0$ ,  $[\theta]_{421} - 67.8$ ,  $[\theta]_{404} 0$ , c 0.025 (360–220 nm)  $[\theta]_{345} + 2425$ ,  $[\theta]_{290} 0$ ,  $[\theta]_{236} + 34,040$ ,  $[\theta]_{220} + 19,390$ .

*General procedure for preparation of  $\pi$ -allyl complexes*

*bis*-Benzonitrile Pd(II)Cl<sub>2</sub> was prepared according to the known procedure<sup>42</sup> from PdCl<sub>4</sub> and

benzonitrile.

The preparation of  $\pi$ -allyl complexes is exemplified by androst-5-ene.<sup>16c</sup> bis-Benzonitrile palladium dichloride (100 mg) in C<sub>6</sub>H<sub>6</sub> (20 ml) was filtered into androst-5-ene (200 mg) in C<sub>6</sub>H<sub>6</sub> (10 ml). At room temperature the deep red colour remained while refluxing for 2 hr over anhyd K<sub>2</sub>CO<sub>3</sub> gave a light yellow solution and some Pd black. Preparative TLC on silica gel gave starting olefin (135 mg) recovered on elution with petroleum ether (40–60). Elution with CHCl<sub>3</sub> gave pale yellow prisms of the androstene complex (40 mg). (Calc for C<sub>18</sub>H<sub>25</sub>PdCl<sub>2</sub>: C, 55.8, H, 7.54. Found: C, 55.72, H, 7.50%). M.p. 145–155° (with decomposition),  $[\alpha]_D -58.3^\circ$ . ORD in CH<sub>2</sub>Cl<sub>2</sub>, c 0.174 (600–340 nm)  $[\Phi]_{600} -222^\circ$ ,  $[\Phi]_{430} -441^\circ$ ,  $[\Phi]_{380} -252^\circ$ , c 0.0174 (340–230 nm)  $[\Phi]_{314} -4010^\circ$ ,  $[\Phi]_{287} -2750^\circ$ ,  $[\Phi]_{275} -3060^\circ$ ,  $[\Phi]_{260} 0^\circ$ ,  $[\Phi]_{255} +1370^\circ$ ,  $[\Phi]_{247} 0^\circ$ ,  $[\Phi]_{230} -5500^\circ$ . CD in CH<sub>2</sub>Cl<sub>2</sub>, c 0.174 (450–340 nm)  $[\theta]_{445} 0$ ,  $[\theta]_{415} -50.5$ ,  $[\theta]_{398} 0$ ,  $[\theta]_{344} +1530$ , c 0.0174 (340–220 nm)  $[\theta]_{318} 0$ ,  $[\theta]_{260} -6330$ ,  $[\theta]_{243-239} 0$ ,  $[\theta]_{225} -5270$ ,  $[\theta]_{220} -2300$ . Application of the procedure to  $\alpha$ -pinene yielded on repetitive TLC separation (CHCl<sub>3</sub> as eluting solvent), two pale yellow crystalline derivatives. The faster running complex from (–)  $\alpha$ -pinene was found identical in every way (TLC and ORD and CD spectra to the complex from (–)  $\beta$ -pinene. Application of the procedure to *cis*- and *trans*-cyclooctene gave in both cases what appeared to be the  $\pi$ -olefin complexes. Reflux over anhyd Na<sub>2</sub>CO<sub>3</sub> in C<sub>6</sub>H<sub>6</sub> gave Pd black and no detectable  $\pi$ -allyl complex on TLC analysis

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