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# Degenerate Cope Rearrangement of Tetracyclo[7.3.1.$0^{2,8}$.$0^{4,12}$]trideca-5,10-diene

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**Abstract**: Tetracyclo[7.3.1.$0^{2,8}$.$0^{4,12}$]trideca-5,10-diene (**3**) is synthesized and partially resolved via reversible ligand exchange in its $^{4}\eta$-diene-tfacac-rhodium(I) complexes **10** and **11** with the $C_2$-chiral bidentate bis-[4(R)-methyl- 5(R)-phenyloxazolinyl]methanide anion. The Cope rearrangment of (+) **3**, converting it into its mirror image, is measured between 39 - 57 °C. The kinetic parameters show that the rate of this rearrangement is $10^8$ times faster than that of the parent hexa-1,5-diene. The strain and rigidity of the cage compound **3** provide an explanation. © 1997 Elsevier Science Ltd.

The degenerate Cope rearrangement of hexa-1,5-diene, a [3,3]-sigmatropic shift in the nomenclature of pericyclic reactions, occurs, as was established three decades ago, via a transition state (or intermediate) with chair conformation[1] and with an activation enthalpy of 33.5 kcal/mol[2]. There is an alternative transition state with the boat conformation that requires ca 11 kcal/mol more of activation enthalpy[3]. The concerted or stepwise mechanism of the reaction is a matter of lasting dispute. A recent calculation[4] finds a tight chair and a loose boat transition state with enthalpies that agree well with the experimental values. No local minimum for a cyclohexa-1,4-diyl intermediate is found on the energy surface of the Cope rearrangement.

Inspite of its higher energy the boat transition state is passed exceedingly fast by some bicyclic dienes possessing the homotropilidene structural element in a fixed boat conformation. Among these are bullvalene[5], barbaralane[6] and semibullvalene **1**[7], compounds referred to sometimes as σ,π-bishomobenzenes. The cyclic 6e-delocalization of the Cope transition state is here already preformed by the overlap of a cyclopropane bond and two π-bonds. However, compounds not having this homoconjugation, such as tricyclo-[6.2.2.$2^{2,5}$]dodeca-1(2),5(6)-diene[8] and hypostrophane[9] **2**, also undergo the Cope rearrangement at room temperature. In the latter compound the bicyclo[6.2.0]decadiene moiety, a homologue of homotropilidene, is fixed in the boat conformation, We set out to extend this strategy to the next higher homologue by undertaking the synthesis of tetracyclo[7.3.1.$0^{2,8}$.$0^{4,12}$]trideca-5,10-diene **3**. In this compound the bicyclo[7.3.0] dodecadiene unit is fixed in the boat conformation by a central zero bridge. The additional methylene bridge brings in chirality which is lost in the $C_s$-symmetric transition state of the Cope rearrangement. The kinetics of the reaction are thus easily obtained.

**1**

**2**

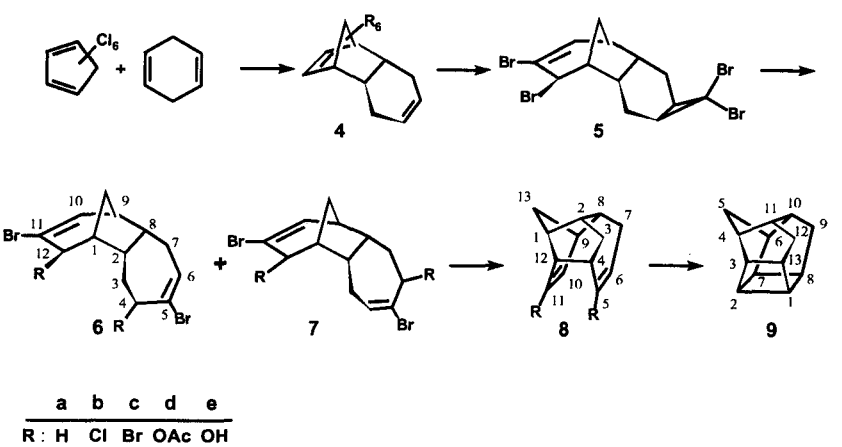
**3**

Starting from hexachlorocyclopentadiene and cyclohexa-1,4-diene (Scheme 1), a cycloaddition followed by a reductive dechlorination with sodium in ethanol gives tricyclo [6.2.1.$0^{2,7}$]undeca-4,9- diene (**4a**)

in good yield[10]. The expansion of both unsaturated bridges in **4a** is achieved in analogy to the synthesis of 1,7-methano[12]annulene[11]: In the first step dibromocarbene is added to both double bonds and as the more highly strained cyclopropane ring is opened under the reaction conditions, *endo,anti*-tetrabromotetracyclo-[7.3.1.$0^{2,8}$.$0^{4,6}$]tridec-10-ene **5** is obtained. The ring opening of the second cyclopropane ring is achieved with silver acetate in boiling acetic acid together with the substitution of both allylic bromines to give the isomeric 2-bromoallyl diacetates **6d**,**7d**. Reduction of these esters to the diols **6e**,**7e** with $LiAlH_4$ and substitution of the hydroxyl groups by bromine with phosphorous tribromide provide the tetrabromides **6c**,**7c**.

The key step in the synthesis of **8a** (= **3**), the intramolecular coupling of the 2-bromoallyl dibromides in **6c**,**7c**, is achieved with tetracarbonyl nickel in DMF[12] in 37% yield. Due to the symmetry of the intermediate bis-π-allyl nickel complex racemic 5,11-dibromotetracyclo[7.3.1.$0^{2,8}$.$0^{4,12}$]trideca-5,10-diene (**8c**) is formed. No cross-coupling occurs for mechanistic as well as thermodynamic reasons. In the final step of the synthesis of **8a** the two bromines in **8c** are removed by reduction with sodium in ethanol.

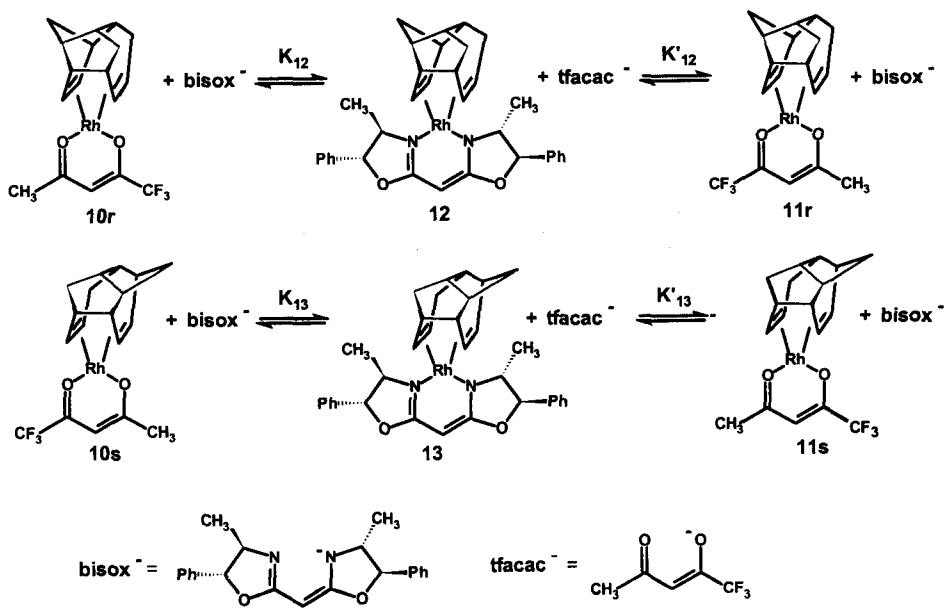
The structure of **8a** was proven by NMR spectroscopy and by chemical means: On irradiation with a mercury lamp in the presence of xanthone the parallel double bonds undergo [2+2]-cycloadditon to form hexacyclo[6.5.0.$0^{2,7}$.$0^{3,13}$.$0^{4,11}$.$0^{6,10}$]tridecane (**9**), a trishomopentaprismane, in high yield.




**Scheme 1**. Synthesis of Tetracyclo[7.3.1.$0^{2,8}$.$0^{4,12}$]trideca-5,10-diene (**8a**)

For resolving the racemic diene **8a** (= **3**) we converted it into a racemic π-complex of rhodium(I) and via reversible ligand exchange with a $C_2$-chiral auxiliar established an equilibrium with a pair of diastereomeric complexes (Scheme 2). Boiling **3** with dicarbonyl-(1,1,1-trifluoropentan-2,4-dionato)rhodium [$(CO)_2$-Rhtfacac] in hexane gives two stereoisomeric $^4$η-dieno-tfacac-rhodium(I) complexes **10** and **11**, both as racemates. Treating **10** and **11** in benzene with 0.5 molar equiv. of bis[4(R)-methyl-5(R)-phenyloxazolinyl]methyl lithium (bisoxLi)[13] at room temperature equilibrates both racemic isomers with the diastereomeric complexes **12** and **13** . The ratios of the equilibrium constants are exponentially correlated to the difference of the free energies of formation of the diastereomers by $K_{12}/K_{13} = K'_{12}/K'_{13} = \exp(-\Delta\Delta G_f/RT)$. However, the diastereomers **12** and **13** are not equilibrated by this method!

After stirring the reaction mixture for 0.5 h at room temperature flash chromatography over silica gel with hexane/ethyl acetate (9 : 1) gives two fractions. The first consists of the starting tfacac-complexes **10** and **11** (68%), in the second fraction a mixture of the diastereomeric bisox-complexes **12** and **13** is obtained (28%). The successful partial resolution by this reversible ligand exchange is first indicated by the rotation $[\alpha]_{589} = -2.57$ (hexane, c 1.49) of the recovered starting complexes. Further proof is given by the $^1$H-NMR spectrum of the mixture of diastereomers **12** and **13:** Their enamide protons give rise to two separate singlets at 5.21 and 5.23 ppm (300 MHz, $C_6D_6$) with a 1.29 : 0.94 ratio of their integrals, indicating 16% de. The yield and the diastereomeric excess together with the amount of bis(oxazolinyl)methyllithium used (0.5 mol equiv.) allow the calculation of the ratio of equilibrium constants $K_{12}/K_{13}$= ( **[12]**·**[10s]** ) / ( **[13]**·**[10r]** ) = 1.56. This value corresponds with a difference of $\Delta\Delta G_f$ = 264 cal/mol between the free energies of formation of the diastereomeric bis(oxazolinyl)methanide-rhodium(I) complexes **12** and **13** .




**Scheme 2**. Resolution of Tetracyclo[7.3.1.$0^{2,8}$.$0^{4,12}$]trideca-5,10-diene via reversible ligand exchange in its tfacac-rhodium complexes **10r,s** and **11r,s** with $C_2$-chiral bis[oxazolinyl]methanide anion (bisox$^-$).

The enantiomerically enriched diene **3** is obtained from the mixture of diasteromeric bisox-complexes **12** and **13** by shaking a solution in methylene chloride at 0 °C with aqueous NaCN. Thereby the yellow olefin complexes are turned into the colorless water soluble complex $Na_3RhH(CN)_5$[14] and **3** is isolated from the organic phase by chromatography over silica gel with pentane. For this separation the column and the eluant must be cooled to below 0 °C. Rotary evaporation of solvent in an ice bath leaves crystalline **3** with the specific rotations given in Table 1 (Experimental Part).

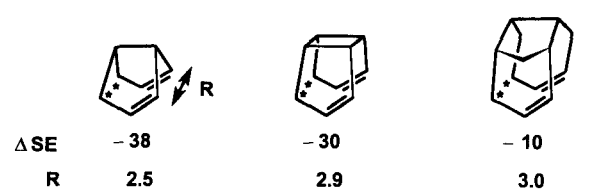
The Cope rearrangement transfers the chiral diene **3** into its mirror image. We measured the kinetics of this process by monitoring the decrease of rotatory power in dodecane solution. The probe was

measured in a double walled polarimeter cell (l = 10 cm, v = 1 ml) kept at constant temperature by circulating water from a thermostat. Between 39 - 57 °C five rate constants were obtained by fitting the measured rotations $\alpha$ to the first order rate equation $\ln(\alpha_0/\alpha) = 2 \cdot kt$. The temperature dependence of the rate constants is given by the Arrhenius equation $\log k = (15.6 \pm 0.5) - (28.9 \pm 0.8) / 2.303 \cdot RT$ ($R = 1{,}987 \cdot 10^{-3}$ kcal $\cdot K^{-1} \cdot mol^{-1}$). Experimental data and further kinetic parameters are collected in Table 2 (Experimental Part).


**Scheme 3**. Degenerate Cope Rearrangement of Tetracyclo[7.3.1.$0^{2,8}$.$0^{4,12}$]trideca-5,10-diene. Absolute configuration not given.

Extrapolation from the Arrhenius equation shows that at 250 °C the Cope rearrangement of **3** is $7 \cdot 10^8$ times faster than that of the parent hexa-1,5-diene via the boat transition state. This dramatic acceleration is due to two effects, i) to the increase of the activation entropy by 13 cal/(K·mol) to 10.6 cal/(K·mol) and ii) to the decrease of the activation enthalpy by 16 kcal/mol to 28.3 kcal/mol. The activation entropy found for the rearrangement of **3** is rather large, however, relative to the activation entropy of –3 cal/(K·mol) for the parent hexa-1,5- diene the increase seems reasonable for the rigid cage diene.

It has been pointed out earlier, that for open chain 1,5-dienes the boat transition state of the Cope rearrangement differs from the chair one by an increase both in enthalpy ($\Delta\Delta H^{\ddagger}$ = ca 12 kcal/mol) and in entropy ($\Delta\Delta S^{\ddagger}$ = ca 11 cal/(K·mol)[3b]. While the reason for the increase in entropy is not clear, the higher enthalpy of the boat transition state results from strain energy. Torsional strain as well as the repulsion of $\pi$-orbitals are greater in the boat form. According to a force field calculation[15] the cage diene **3** incorporates 35 kcal/mol of strain energy (SE) and the breaking of the central bond to generate two noninteracting allylic radicals is accompanied by a strain release of $\Delta SE = -10$ kcal/mol (Scheme 4). The diradical derived from **3** is too open to represent well the boat transition state, for which the distance R = 2.2 Å has been calculated [4]. However, a strain release of $\Delta SE = -5$ kcal/mol in attaining it seems reasonable and would agree with the activation enthalpy found.




**Scheme 4**. Strain release $\Delta$SE [kcal/mol] on forming diradicals from cage dienes **1**, **2**, and **3** and distance R [Å] between their terminal atoms.

The diradical model can also be used to estimate the strain release in the transition states of semibullvalene and hypostrophane. As shown in Scheme 4, much more strain is lost on the formation of their diradicals than is in the case of **3**, and the order of $\Delta$SEs relates well to the rates of their Cope rearrangement.

## EXPERIMENTAL

Thin-layer chromatography (tlc) was performed on Polygram SIL G/254 UV foils (Machery-Nagel, Düren), $R_f$ values refer to tlc analyses with the eluant given. For flash chromatography (flc) silica gel Silitech 32-64 60A (ICN Eschwege) was used. Melting points were determined in open capillaries with a Tottoli apparatus (Büchi Flawil), they are uncorrected. NMR spectra were taken on a Bruker AM 300 spectrometer at 300 ($^1$H) and 75.5 MHz ($^{13}$C) in $CDCl_3$, other solvent are noted. Chemical shifts are in δ ppm relative to internal TMS. Signals were assigned by C-H COSY and NOE methods. Multiplicities and the position of protons are abbreviated as follows: s (singlet), d (doublet), dd (doublet of doublets), t (triplet), m (multiplet), br (broad), A of AB (A part of AB system), *x* (*exo*), *n* (*endo*). Optical rotations were determined with the polarimeter 241 (Perkin-Elmer, Überlingen). Mass spectra were obtained from either INCOS 50 or H-SQ 30 (both Finnigan-MAT).

**1,8,9,10,11,12-Hexachlorotricyclo[6.2.1.0$^{2,7}$]undeca-4,9-diene (4b)**: Hexachlorocyclopentadiene (40 ml, 68.1 g, 0.250 mol) and cyclohexa-1,4-diene (100 ml, 84.7 g, 1.06 mol) are heated together with a trace of 4-tert.-butylcatechol (50 mg) under reflux in an argon atmosphere. After distilling off the excess of cyclohexadiene, the residue is fractionated *in vacuo* to yield **4b** (70.5 g, 80%): bp 122 °C (0.2 Torr),fp 66 °C.- $^1$H-NMR: δ = 5.83 (t, 2 H), 2.02 (m, 2 H), 2.6 - 1.7 (AB, 4 H, $^2J$ = 16.0 Hz, $CH_2$).

**Tricyclo[6.2.1.0$^{2,7}$]undeca-4,9-diene (4a)**: In a 3-necked 2 l flask fitted with a stirrer and reflux condenser a solution of **4b** (33.15 g, 0.094 mol) in ethanol (800 ml) is heated to reflux. The oil bath is removed and Na (92.3 g, 4.0 mol) is added in pieces over 4 h at such a rate to maintain boiling. The reaction mixture is heated to reflux for an additional h and hydrolyzed with water (0.5 l). Two phases are formed and the lower one, a concentrated aqueous solution of NaCl and NaOH is discarted. The organic phase is diluted with water (300 ml) and extrac- ted with three portions (100 ml) of pentane. The extract is washed with brine (200 ml), dried ($MgSO_4$) and concentrated. The combined crude product of three preparations is distilled *in vacuo* over a Vigreux column (10 x 1.5 cm) to give tricyclo[6.2.1.0$^{2,7}$]undeca-4,9-diene as a colorless oil (28.8 g, 69.9%). **4a**: bp 86 - 88 °C (15 Torr).- $^1$H-NMR: δ = 6.08 (t, 2 H), 5.65 (m, 2 H), 2.71 (br s, 2 H), 2.29 (br s, 2 H), 1.90 (br AB, 4 H, $^2J$ = 18 Hz, allylic $CH_2$), 1.52 (t, 2 H, $CH_2$).

**5,5,11,12-Tetrabromotetracyclo[7.3.1.0$^{2,8}$.0$^{4,6}$]tridec-10-ene (5)**: In a 3 necked 11 flask equipped with a stirring motor and an air cooled condenser is placed a solution of **4a** (28.8 g, 0.195 mol) in bromoform (210 ml) together with freshly recrystallized triethylbenzylammonium chloride (TEBA, 2.5 g, 11 mmol) and 50% aqueous NaOH (190 ml, 3.624 mol). The mixture is shaded, stirred rapidly and in the beginning cooled with a water bath. When no more heat is evolved stirring is continued at room temperature for 90 h, whereafter the monoadduct no longer can be detected by tlc. The reaction mixture is partitioned between water (800 ml) and chloroform (200 ml) and the aqueous phase is washed with 3 portions (200 ml) of chloroform. The combined organic phases are washed with water (500 ml) and with brine (500 ml) and dried ($MgSO_4$). The haloform solvents are distilled off *in vacuo*, keeping the bath below 100 °C. The tarry residue is dissolved in methylene chloride (100 ml) and deposited on silica gel (60 g) in a rotary evaporator. The coated silica gel is placed on top of a column (8 x 7.5 cm) of silica gel in a dropping funnel with pressure equilibration. The funnel is connected to a 1 l flask and pentane (500 ml) is passed through the silica gel. After placing a reflux condenser on top of the funnel, the flask is heated and the pentane refluxing from the condenser passes the column and elutes the product continuously. During the first 6 h contaminations exit that are followed by product during the next 60 h . Concentration of the eluate leaves light green crystals of **5** which are recrystallized from hexane ( 68.1 g, 70.5%): fp 156 -157 °C.- $^1$H-NMR: δ = 6.22 (dd, 1 H), 4.62 (d, 1H), 2.83 (br s, 1 H), 2.51 (br s , 1 H), 2.32 (A of AB, $^2J$ = 16 Hz, 1 H), 2.17, (m, 4 H), 1.70, (m, 2 H), 1.64, (B of AB, 1 H), 0.88, (m, 1 H), 0.63

(m, 1 H).- $^{13}$C-NMR: δ = 138.37, 121.67, 57.75, 46.41, 42.32, 40.81, 40.26, 37.67, 31.06, 29.65 (2C), 24.21, 23.69.

**4,12-Diacetoxy-5,11-dibromotricyclo[7.3.1.0$^{2,8}$]trideca-5,10-diene (6d)** and **6,12-diacetoxy-5,11-dibromotricyclo[7.3.1.0$^{2,8}$]trideca-4,10-diene (7d)**: In a 3 necked flask equipped with a stirring motor and reflux condenser **5** (44.83 g, 92 mmol) and silver acetate (46.0 g, 276 mmol) in acetic acid (0.5 l) are refluxed for 117 h in the dark. After cooling, ether (0.5 l) is added and the precipitated silver salts are collected on a filter and washed with ether. The filtrates are evaporated and the residue is taken up in ether and washed with saturated aqueous $NaHCO_3$ (0.5 l), water (0.25 l) and brine and dried over $MgSO_4$. Evaporation leaves a dark residue which is taken up in methylene chloride and filtered through a column (9 x 5 cm) of alumina. The filtrate is concentrated to an orange oil which is flash chromatographed in four portions with hexane/ethyl acetate (9 : 1) over silica gel. Two fractions are collected, leaving after evaporation colorless glasses. **7d** (5.8 g, $R_f$ = 0.18), **6d** (11.89 g, $R_f$ = 0.10). The crude acetates are reduced together in the next step, their structures were deduced from that of the resulting alcohols .

**5,11-Dibromotricyclo[7.3.1.0$^{2,8}$]trideca-5,10-diene-4,12-diol (6e)** and **5,11-dibromotricyclo[7.3.1.0$^{2,8}$]trideca-4,10-diene-6,12-diol (7e)**: To the stirred and ice-cooled suspension of $LiAlH_4$ (7.28 g, 0.192 mol) in ether (250 ml) are added over 30 min the combined acetates **6d** and **7d** (17.10 g, 43.6 mmol) in ether (100 ml). After heating to reflux for 2 h the reaction mixture is cooled, hydrolyzed with 1 M $K_2CO_3$ (34 ml) and stirred over night. The crystalline precipitate of inorganic salts is filtered off and extracted with ether in a Soxhlet apparatus for 10 h. The filtrate and the extract are combined and evaporated, yielding the product as a colorless glass (13.35 g, 84%). For the determination of product ratio and structures a part of the crude product was flash chromatographed with methylene chloride/acetonitril (9 : 1) over silica gel. Two fractions (0.33 g and 0.68 g) were collected and recrystallized from chloroform.

**6e:** $R_f$ = 0.43; fp 179 °C.- $^1$H-NMR: δ = 6.32 (d, 1 H, 10-H), 6.27 (dd, 1 H, 6-H), 4.19 (m, 1 H, 4-H), 3.91 (m, 1 H, 12-H), 2.58 (m, 1 H, 8-H), 2.52 (m, 2 H, 1,9-H), 2.44 (d,1 H, 4-OH), 2.24 (m, 1 H, 2-H), 2.19 (A of AB, 1 H, 7-H), 2.12 (d, 1 H, 12-OH), 2.06 (B of AB,1 H, 7-H), 1.99 (A of AB, 1 H, 13-H$_x$), 1.50 (B of AB, 1 H, 13-H$_n$).- $^{13}$C-NMR: δ = 137.10 (C-10), 132.28 (C-6), 130.10 (C-5), 124.20 (C-11), 75.76 (C-4), 72.54 (C-12), 45.94 (C-1), 43.09 (C-9), 40.60 (C-8), 40.20 (C-2), 33.26 (C-3), 30.94 (C-13), 26.71 (C-7).

**7e**: $R_f$ = 0.29; fp 168 °C.- $^1$H-NMR: δ = 6.33 (dd, 1 H, 10-H), 6.24 (m, 1 H, 4-H), 4.40 (m, 1 H, 6-H), 3.92 (m, 1 H, 12-H), 2.64 (m, 2 H, 2,8-H), 2.55 (m, 1 H, 1-H), 2.45 (m, 1 H, 9-H), 2.36 (d, 1 H, 6-OH), 2.07 (m, 2 H, 3-H), 2.05 (m, 1 H, 12-OH), 2.00 (m, 1 H, 7-H), 1.89 (A of AB, 1 H, 13-H$_x$), 1.47 (B of AB, 1 H, 13-H$_n$).- $^{13}$C-NMR: δ = 137.61 (C-10), 132.36 (C-4), 129.49 (C-5), 124.19 (C-11), 73.96 (C-6), 72.70 (C-12), 46.37 (C-1), 43.07 (C-9), 41.26 (C-2), 37.45 (C-8), 32.11 (C-7), 30.63 (C-13), 27.08 (C-3).

**4,5,11,12-Tetrabromotricyclo[7.3.1.0$^{2,8}$]trideca-5,10-diene (6c)** and **5,6,11,12-tetrabromotricyclo[7.3.1.0$^{2,8}$]trideca-4,10-diene (7c)**: To the 1 : 2 mixture of the diols **6e**,**7e** (2.52 g, 6.92 mmol) in ether (100 ml) is added $PBr_3$ (1.44 g, 5.32 mmol). The reaction mixture is stirred for 3 h at 0 °C, for additional 40 h at room temperature and is then hydrolyzed with aqueous 0.32 M $K_2CO_3$ (50 ml, 16 mmol). The aqueous phase is extracted 3 times with ether (20 ml) and the combined organic phases are washed with brine and dried over $MgSO_4$. The crystals obtained after evaporation are flash chromatographed with cyclohexane over silica gel and used as a mixture (2.88 g, 85%) in the next step.

**5,11-Dibromotetracyclo[7.3.1.0$^{2,8}$.0$^{4,12}$]trideca-5-10-diene (8c)**: The isomeric tetrabromides **6c**,**7c** (2.88 g, 5.88 mmol) are dissolved in dry dimethyl formamide (DMF, 50 ml) and placed in a dropping funnel with

pressure equilibration. The funnel is attached to a 3 necked 0.5 l flask with reflux condenser and magnetic stirring bar. Dry DMF (225 ml) is poured into the flask and solvent as well as solution are deaerated and kept under argon. Tetracarbonyl nickel (4 ml, 5.31 g, 31.1 mmol) is filled from a steel cylinder into a Schlenk tube that is cooled with dry ice and purged with argon. **CAUTION**: tetracarbonyl nickel is volatile, combustible in air and extremely toxic! Using a steel capillary and septa, the nickel carbonyl is transferred by argon pressure below the surface of the DMF in the flask. The septa are replaced by stop cocks, a bubble counter is attached to the reflux condenser and the contents of the flask is stirred and heated to 50 °C. In the course of 4 h the solution of tetrabromides is added. The reaction mixture, turning green and evolving CO, is kept for further 6 h at 50 °C, whereafter the gas evolution has ceased. After cooling to room temperature, the reaction mixture is diluted with water (1 l) and extracted with ether (3x300 ml). The organic phases are washed with water (2 x 1 l) and brine (0.5 l) and dried ($MgSO_4$). The ether and an excess of tetracarbonyl nickel are distilled off into a receiver with a trap attached, both cooled with dry ice. The distillate is treated with $Br_2$ in $CCl_4$ to oxidize the nickel carbonyl. The green solid residue in the stillpot is dissolved in methylene chloride, deposited on silica gel (4 g) and filtered with hexane through silica gel (5 x 3.5 cm). Concentration and recrystallization from hexane yields **8c:** 0.72 g (37 %); fp 125-126 °C.- $^1$H-NMR: δ = 6.52 (dd, 1 H, 10-H), 6.99 (dd, 1 H, 6-H), 3.59 (AB, 2 H, 4,12-H), 2.51 (m, 1 H, 9-H), 2.44 (m, 2 H, 2,8-H), 2.34 (m, 1 H, 1-H), 2.26, 2.05 (AB, 2 H 2,7-H), 2.08, 1.93 (AB, 2 H, 3-H), 1.68, 1.36 (AB, 2 H, 13-H).- $^{13}$C-NMR: δ = 137.18 (C-10), 131.08 (C-6), 124.06 (C-11), 123.15 (C-5), 56.42 (C-12), 55.92 (C-4), 49.48 (C-1), 48.39 (C-2), 43.40 (C-8), 43.20 (C-9), 37.87 (C-13), 35.75 (C-3), 31.20 (C-7).

**Tetracyclo[7.3.1.0$^{2,8}$.0$^{4,12}$]trideca-5,10-diene (8a = 3).** In a 2 necked 25 ml flask with a reflux condenser **8c** (0.63 g, 1.91 mmol) in dry ethanol (10 ml) is heated to 80 °C under an argon atmosphere.In the course of 0.5 h Na (1.10 g, 47.9 mmol) is added and the reaction mixture is heated for another 2 h. The warm mixture is carefully quenched with water (5 ml), cooled and extracted with pentane (3 x 10 ml). The combined extracts are washed with water (10 ml) and brine (10 ml) and dried ($MgSO_4$). The solid residue of evaporation is sublimed at 60 °C (16 Torr) to give **8a**: 0.285 g (87%); fp 208 - 209 °C.- $^1$H-NMR: δ = 6.19 (m, 1 H, 10-H), 6.00 (m, 1 H, 6-H), 5.44 (m, 1 H, 5-H), 5.09 (m, 1 H, 11-H), 3.13 (AB, 2 H, 4,12-H), 2.41 (m, 3 H 2,8,9-H) 2.26, 2.08 (AB, 2 H, $CH_2$), 2.25 (br s,1 H, 1-H), 1.91, 1.86 (AB, 2 H, $CH_2$), 1.63, 1.16 (AB, 2 H, 13-H).- $^{13}$C-NMR: δ = 134.84 (C-10), 133.55 (C-5), 131.78 (C-11), 128.46 (C-6), 48.92, 43.53, 41.05, 47.63 (C-1), 46.42 (C-12), 44.68 (C-4), 38.53 (C-13), 35.85 (C-3), 30.70 (C-7).- MS (70 eV), *m/z* (%): 172 (16) [$M^+$], 129 (24) [$C_{10}H_9^+$], 91 (71) [$C_7H_7^+$], 79 (100) [$C_6H_7^+$], 77 (86) [$C_6H_5^+$].- HRMS calcd.for $C_{13}H_{16}$ 172.1252, found 172.1252.

**Hexacyclo[6.5.0.0$^{2,7}$.0$^{3,13}$.0$^{4,11}$.0$^{6,10}$]tridecan (9).** The solution of **8a** (35 mg, 0.20 mmol) and a few crystals of xanthone in $CDCl_3$ is deaerated in a NMR tube and kept by a clamp in a 250 ml beaker with water. The water is exchanged continuously and the solution is irradiated with a sun lamp (Osram Vitalux). After 3 h olefinic protons no longer can be detected by $^1$H-NMR. The solvent is evaporated and the residue is filtered with pentane through silica gel (4 x 1 cm) and sublimed at 60 °C (16 Torr). **9**: 30 mg (86%); fp 232 - 235 °C (subl.).- $^1$H-NMR: δ = 3.04 (m, 2 H, 8,13-H), 2.83 (m, 2 H, 3,7-H), 2.57 (m, 2 H, 10,11-H), 2.45 (m, 1 H, 2-H), 2.41 (m, 2 H, 4,6-H), 2.25 (m, 1 H, 1-H), 2.05 (A of AB, $^2J$ = 13.7 Hz, 2 H, 9,12-H$_n$), 1.64 (A of AB, 1 H, 5-H), 1.54 (B of AB, 2 H, 9,12-H$_x$), 1.42 (B of AB, $^2J$ = 11.7 Hz, 1 H, 5-H).- $^{13}$C-NMR: δ = 46.58 (C-10,11), 46.09 (C-8,13), 45.75 (C-4,6), 41.89 (C-3,7), 33.20 (C-2), 32.68 (C-9,12), 28.14 (C-5), 24.90 (C-1).- MS (70 eV), *m/z* (%): 172 (23) [$M^+$], 129 (48) [$C_{10}H_9^+$], 91 (76) [$C_7H_7^+$], 79 (100) [$C_6H_7^+$].

**η$^4$-Tetracyclo[7.3.1.0$^{2,8}$.0$^{4,12}$]trideca-5,10-diene(1,1,1-trifluoroacetylacetonato)rhodium(I)** stereoisomers **10** and **11**. Dicarbonyl(1,1,1-trifluoroacetylacetonato)rhodium(I)[16] (0.43 g, 1.38 mmol) and **8a** (0.22 g, 1.28

mmol) are dissolved in hexane (1 ml) and heated under argon for 21 h to 70 °C. The solvent is evaporated and unreacted educts sublimed off at 60 °C (16 Torr). The residue is recrystallized from hexane yielding yellow needles of **10** and **11**: 0.49 g (90%); fp 149 -150 °C.- $^1$H-NMR ($C_6D_6$): δ = 5.50 (s, 1 H, enolate-H), 4.73, 4.67 (2 m, 1 H, 10-H), 4.40, 4.35 (2 m, 1 H, 11-H), 4.32 (m, 1 H, 5-H), 3.96 (m, 1 H, 6-H), 3.27 (m, 1 H, 4-H), 3.17 (m, 1 H, 12-H), 2.42, 2.35 (2 m, 1 H, 1-H), 2.16 (A of AB, 1 H, 7-H), 2.05 (m, 1 H, 8-H), 1.89 (m, 1 H, 2-H), 1.83 (m, 1 H, 9-H), 1.52, 1.51 (2 s, 3 H, $CH_3$), 1.50 (B of AB, 1 H, 7-H), 1.38, (m, 2 H, 3-H), 1.39, 1.33 (2 A of AB, 1 H, 13-H), 1.12, 1.07 (2 B of AB, 1 H, 13-H). Equal integrals for separated signals of the same proton of the olefinic ligand indicate the presence of a 1:1 mixture of **10** and **11**.- MS (70 eV,EI), *m/z* (%): 428 (100) [$M^+$], 275 (26) [M - tfacac$^+$], 195 (52) [$RhC_7H_8^+$], 103 (16) [$Rh^+$].

**Bis[(4R, 5R)-4-methyl-5-phenyl-oxazolinyl]methane**[13]. (-)-Norpseudoephedrine (5.91 g, 39.1 mmol) and diethyl malonate (3 ml, 3.17 g, 19.8 mmol) in dry xylene (150 ml) are heated to reflux for 11 h. Forming water is collected in a separator attached between the flask and the condenser. After cooling dibromodimethylstannane (123 mg, 0.40 mmol) is added and the reaction is continued for 48 h under reflux. The mixture is concentrated in a rotary evaporator and the oily residue is flash chromatographed with ethyl acetate over silica gel (12 x 3.5 cm). The product is isolated as a colorless oil (6.72 g, 52.4%).

**$^4$η-Tetracyclo[7.3.1.0$^{2,8}$.0$^{4,12}$]trideca-5,10-diene-bis[(4R),(5R)-4-methyl-5-phenyl-oxazolinyl]methanide rhodium(I)** diastereomers **12** and **13**. The solution of bis(oxazolinyl)methane (112 mg, 0.40 mmol) in dry benzene (2 ml) is given into a 2 necked 25 ml flask equipped with a septum and a three way stopcock. After deaerating, the solution is kept under argon and 1.6 M *n*-butyllithium in hexane (0.2 ml, 0.32 mmol) is added. The mixture is stirred for 5 min at room temperature, thereafter a solution of the isomeric tfacac rhodium complexes **10** and **11** (274 mg, 0.64 mmol) in benzene (4 ml) is added. The reaction mixture is stirred for 0.5 h at room temperature, concentrated with a rotary evaporator and flash chromtographed with hexan/ethyl acetate (9 : 1) over silica gel (12 x 3.5 cm). Two fractions are collected, yielding **(-)10,11** (181.2 mg, 63%, $R_f$ = 0.8) and **12,13** (112 mg, 27.5%, $R_f$ = 0.43). **12,13**: yellow crystals, fp 212 °C (dec).- $^1$H-NMR ($C_6D_6$): δ = 7.18 (m, ph-H), 7.00 (m, ph-H), 5.23 (s, enamide H), 5.21 (s, enamide H), 4.80 (m, benzylic H), 4.77 (m, benzylic H), 4.37 - 3.64 ( 8 overlapping ms, olefinic H), 3.44 - 1.07 (overlapping ms). The ratio of integrals δ 5.23/5.21 = 1.29 : 0.94 indicates 16% de. (-)-**10,11**: $[\alpha]_{589}$ = –2.57 (hexane, c 1.49).

**(+)-Tetracyclo[7.3.1.0$^{2,8}$.0$^{4,12}$]trideca-5,10-diene ((+)-3)**. The diastereomeric bis(oxazolinyl)methaniderhodium complexes **12** and **13** (112 mg, 0.184 mmol, 16% de) in methylene chloride (3 ml) are shaken in a separatory funnel with an aqueous solution of NaCN (10%, 10 ml) together with some crushed ice. After 2 min the yellow organic phase has turned colorless. The phases are separated and the aqueous phase is extracted with cold methylene chloride (3 x 5 ml). The combined organic phases are washed with cold brine and concentrated at 0 °C. The residue is taken up in cold pentane and filtered through a column (5 x 1.5 cm) with silica gel, cooled with dry ice/isopropanol in an outer jacket. The filtrate is evaporated in an ice bath leaving crystalline **(+)-3** (25.4 mg, 75.2%) whose specific rotations are given in Table 1. Using the same procedure, the tfacac-rhodium complexes **(-)-10,11** (181 mg, 0.422 mmol) recovered from the preparation of **12,13** are decomposed to give **(-)-3:** 57.6 mg (79%).- $[\alpha]_{589}$ = – 0.57 (hexane, c 2.83).

**Table 1**.Specific Rotation of (+)-Tetracyclo[7.3.1.0$^{2,8}$.0$^{4,12}$]trideca-5,10-diene (**3**) of 16% ee in Dodecane (c 2.54)

| λ [nm] | 589 | 578 | 546 | 436 | 405 | 365 |
|---|---|---|---|---|---|---|
| [α] [deg cm$^{-2}$ g$^{-1}$] | 1.44 | 2.05 | 2.02 | 4.70 | 10.17 | 22.83 |

*Kinetic measurement.*

The solution of (+)-**3** or (-)-**3** in dodecane (c 0.4, 1.0 resp.) is given into a double walled polarimeter cell with quartz windows (10 cm, 1 ml), kept at constant temperature by circulating water from a thermostat through its outer jacket. When temperature equilibration is reached, the rotation of the probe is measured in a polarimeter (Perkin-Elmer 241) at $\lambda$ = 365 nm. The mean of the rotation over 50 s is printed out continuously. 10 - 20 of these values, covering two half-lives, are used to determine the rate constant k of the first order rate equation $\lg(\alpha_0/\alpha_t) = 2 \cdot k \cdot t$. Complete racemization after t > 10 half-lives is verified and the temperature in the cell is measured at this point with a thermistor thermometer. The pairs of values ($\alpha$; t) used for the determination of the rate constants at five temperatures from 39 - 57 °C are given in Table 2, together with the rate constants at these temperatures and the kinetic parameters obtained from a least squares fit to the Arrhenius equation.

**Table 2.** Experimental Data and Kinetic Parameters for the Racemization of Tetracyclo-[7.3.1.$0^{2,8}$.$0^{4,12}$]trideca-5,10-diene **(3)** in Dodecane

| T = 39.4 °C | | T = 43.4 °C | | T = 47.9 °C | | T = 52.4 °C | | T = 57.1 °C | |
|---|---|---|---|---|---|---|---|---|---|
| t[s] | α [°] | t[s] | α [°] | t[s] | α [°] | t[s] | α [°] | t[s] | α [°] |
| 0.000 | 0.056 | 0.000 | 0.027 | 0.000 | 0.069 | 0.000 | 0.050 | 0.000 | −0.105 |
| 2140.00 | 0.052 | 2140.00 | 0.024 | 535.000 | 0.064 | 267.000 | 0.046 | 214.000 | −0.092 |
| 4280.00 | 0.047 | 4280.00 | 0.021 | 1070.00 | 0.059 | 535.000 | 0.043 | 428.000 | −0.082 |
| 6420.00 | 0.042 | 6420.00 | 0.019 | 1605.00 | 0.055 | 802.000 | 0.040 | 642.000 | −0.073 |
| 8560.00 | 0.039 | 8560.00 | 0.016 | 2140.00 | 0.050 | 1070.00 | 0.038 | 856.000 | −0.063 |
| 10700.0 | 0.035 | 10700.0 | 0.013 | 2675.00 | 0.047 | 1338.00 | 0.035 | 1070.00 | −0.057 |
| 12840.0 | 0.032 | 12840.0 | 0.011 | 3210.00 | 0.043 | 1605.00 | 0.035 | 1284.00 | −0.050 |
| 14980.0 | 0.029 | 14980.0 | 0.010 | 3745.00 | 0.039 | 1873.00 | 0.033 | 1498.00 | −0.044 |
| 17120.0 | 0.027 | 17120.0 | 0.008 | 4280.00 | 0.036 | 2140.00 | 0.031 | 1712.00 | −0.038 |
| 19260.0 | 0.024 | 19260.0 | 0.007 | 4815.00 | 0.033 | 4008.00 | 0.029 | 1926.00 | −0.033 |
| 21400.0 | 0.022 | | | 5350.00 | 0.031 | 2675.00 | 0.027 | 2140.00 | −0.029 |
| 23540.0 | 0.020 | | | 5885.00 | 0.029 | 2943.00 | 0.025 | 2354.00 | −0.024 |
| 25680.0 | 0.018 | | | 6420.00 | 0.026 | 3210.00 | 0.021 | | |
| 27820.0 | 0.017 | | | 6955.00 | 0.024 | 3478.00 | 0.020 | | |
| 32100.0 | 0.014 | | | 7490.00 | 0.022 | 3745.00 | 0.019 | | |
| 36380.0 | 0.012 | | | 8025.00 | 0.021 | 4013.00 | 0.017 | | |
| 40660.0 | 0.010 | | | 8560.00 | 0.019 | 4280.00 | 0.016 | | |

| $k \cdot 10^5$ [$s^{-1}$] | | | | |
|---|---|---|---|---|
| 2.163 ± 0.010 | 3.441 ± 0.091 | 7.555 ± 0.045 | 13.33 ± 0.10 | 25.35 ± 0.19 |

| $E_a$ [kcal/mol] | log A | $\Delta H^{\ddagger}$ [kcal/mol] | $\Delta S^{\ddagger}$ [cal/mol.K] | $\Delta G^{\ddagger}$ [kcal/mol] |
|---|---|---|---|---|
| 28.91 ± 0.76 | 15.55 ± 0.52 | 28.32 ± 0.76 | 10.6 ± 2.4 | 25.16 ± 1.04 |

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