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CHIRAL AND DIASTEREOISOMERIC RHODIUM(I) COORDINATION COMPOUNDS WITH CARVONE AS BIDENTATE LIGAND

V. SCHURIG
Department of Chemistry, University of Tübingen, Auf der Morgenstelle, D 74 Tübingen (W.-Germany)

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Summary

The chiral dienone *p*-mentha-6,8-dien-2-one (carvone) coordinates readily with rhodium(I) to form complexes of pronounced stability. Novel diastereoisomeric planar coordination compounds of rhodium(I) containing two chiral bidentate ligands have been prepared for the first time. The synthesis of the compounds is simple, and the yields are high.

Introduction

Following the initial report on the preparation of dimeric *cis,cis*-cycloocta-1,5-dienerhodium(I) chloride [1], a large number of rhodium coordination compounds with non-conjugated diolefins of suitable geometry have appeared [2—9]. In the search for chiral rhodium coordination compounds containing readily available, stable optically active bidentate ligands, we found that L-*p*-mentha-6,8-dien-2-one (carvone) has a pronounced propensity to coordinate with the monovalent rhodium ion.

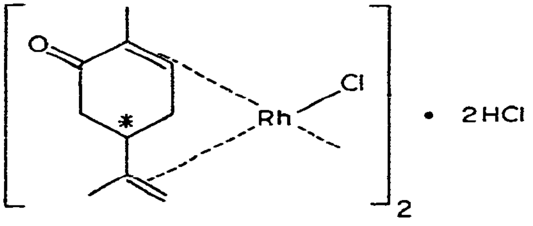
Results and discussion

If an ethanolic solution of $RhCl_3 \cdot 3H_2O$ is refluxed for 2 h in the presence of (*R* or *S*)-carvone, a complex (I) with a ratio of carvone, rhodium and chlorine of 1/1/2 is formed in high yield. (I) is soluble in common organic solvents and is air-stable up to 210°C. The complex may also be obtained by displacement of ethene from $(C_2H_4)_4Rh_2Cl_2$ by carvone in chloroform or benzene.

Coordination of carvone with rhodium(I) is evident from a decrease in the IR double bond stretching frequencies observed for (I) (i.e. 1500 and 1465 cm^{-1}). The unchanged absorption band at 1665 cm^{-1} suggests that the carbonyl group is not involved in the chelate bonding. Strong interaction of the diolefin with rhodium(I) is also illustrated by NMR data. Thus, the ^1H NMR spectrum of (I) (in $CDCl_3$) shows an upfield shift for the cyclic olefinic proton (τ 4.92; carvone, τ 3.38) and for the acyclic olefinic protons (τ 6.85 and τ 7.00; carvone, τ 5.32). In contrast to carvone, the terminal protons are non-equivalent in the complex. The two methyl groups in (I) absorb at higher (τ 8.59) and lower (τ 8.17) field relative to carvone (τ 8.26 and 8.28). The difference of the methyl group absorbances is attributed to different steric and electronic requirements of the two olefin—metal bonds (vide infra).

The sign of the optical rotation of carvone is reversed on complex formation with rhodium(I). The absence of isomerisation and racemisation of carvone upon coordination is indicated by complete recovery of the original ligand by cyanide displacement. The chiral ligand carvone may also be displaced from (I) by an excess of cycloocta-1,5-diene in a homogeneous exchange reaction in chloroform or ethanol. The cycloocta-1,5-dienerhodium(I) chloride dimer formed has been isolated from ethanol and it was shown to be identical with an authentic sample by IR [1]. The kinetics of the exchange reaction can be monitored by polarimetry. Thus, the initial change of the optical rotation was —7 deg sec^{-1} when a molar excess (10/1) of cycloocta-1,5-diene was added to a $2\cdot 10^{-3}$ *M* solution of (I) containing (*R*)-carvone, $[\alpha]_D^{20}$ + 460°, in chloroform at 20°C.

The experimental results and the mass spectrum (molecular ion peak at 576) accord with a dimeric square planar structure for (I), as established for cycloocta-1,5-dienerhodium(I) chloride by X-ray structural analysis [10]. However, the rhodium/chlorine ratio of 1/2, as established by elemental analysis of solid (I), suggests the possible formation of a di-HCl-adduct of the dimer. No spectroscopic evidence on the mode of the bonding of the second chlorine has so far been obtained.

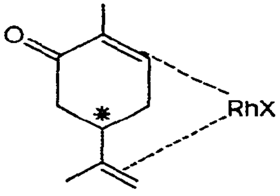


(I)

(I) can undergo typical bridge-splitting reactions. Thus, for example, reaction of (I) with sodium acetylacetonate yields carvonerhodium(I) acetylacetonate (II), which may also be obtained by displacement of ethylene by carvone from $(C_2H_4)_2Rh(acac)$. Reaction of (I) with sodium cyclopentadienide affords carvonerhodium(I) cyclopentadienide (III). Reaction of (I) containing (*R* or *S*)-carvone with barium(II) bis(3-trifluoroacetyl-(1*R*)-camphorate) [11] leads to novel stable diastereoisomers (IV), containing two chiral bidentate terpenoide ligands bonded to rhodium(I). The diastereoisomers (IV) exhibit the expected differences in their physical properties. Spectral differences were observed in the proton nuclear magnetic resonances of the methyl groups (about 2.5 Hz).

In view of the thermodynamic stability of (I—IV) the reaction of dipentene

(*R*,*S*-limonene) with rhodium(I) has been reinvestigated [1]. Although displacement of ethene from $(C_2H_4)_2Rh(acac)$ and reaction of $RhCl_3 \cdot 3H_2O$ did occur, no stable products were isolated.



(II) X = Acetylacetonate
(III) X = Cyclopentadienide
(IV) X = 3-Trifluoroacetyl-
-(1R)-camphorate

The marked stability of the carvone—rhodium(I) bond is rather unexpected. Molecular models show that no parallel arrangement of the two double bonds can be attained in the molecule as is necessary for a maximum orbital overlap with the metal in the square planar configuration [10]. In addition, the two methyl groups impose a considerable steric hindrance on the C=C double bonds of carvone. Di- and trisubstitution at the double bond, however, constrains coordination with rhodium(I) severely, as has been established for monoolefins [12,13].

Metal *d*- to olefin π-back-bonding has been identified as the dominant factor in determining the thermodynamic stability of the metal—olefin bond in square planar rhodium(I) olefin complexes [7,12,14]. π-Back-bonding from *d*-orbitals of rhodium(I) onto π^*-orbitals of the conjugated dienone C=C double bond of carvone may in fact occur more readily than in the case of dipentene. Conversely, in making up the loss of charge at the metal, a strong σ-bond could arise between the isopropenyl C=C double bond and the metal. Overlap associated with the σ-portion of the bond is not affected by a deviation from the perpendicular arrangement of the double bond axis to the coordination plane. The molecular geometry of (I) is therefore suggested to resemble that of dipenteneplatinum(II) dichloride [15]. In this molecule the cyclic double bond acquires a perpendicular position to the square coordination plane, whereas the axis of the isopropenyl double bond is inclined at an angle of 62° to the intersection of the sp^2 double bond plane and the dsp^2 coordination plane [15].

Conclusion

Use of carvone as a novel diolefinic ligand for rhodium(I) may contribute to the further elucidation of the nature and stability of the diolefin—metal bond. The presence of the free carbonyl group provides a reactive center allowing derivatisation, polymer-linking, and the study of the reactivity of the coordinated ligand. Aspects associated with the chirality of the ligand are being currently studied.

Experimental

(R)-p-Mentha-6,8-dien-2-one, (—)-carvone, $[\alpha]_D^{20}$ —62° and (S)-p-mentha-6,8-dien-2-one, (+)-carvone, $[\alpha]_D^{20}$ + 62° were obtained from Fluka, AG, and used without further purification. $RhCl_3 \cdot 3H_2O$ (Rh 38.85%) was provided by Johnson, Matthey Ltd. Solvents used were E. Merck reagent grade. IR absorption spectra were recorded with a Perkin—Elmer Spectrophotometer (221), and NMR spectra were measured with a Varian A 60A instrument at room temperature. Optical rotations were obtained at 20°C with a Carl Zeiss Polarimeter (OL D/5) at the Hg lines 578 and 546 nm and extrapolated to the sodium D line. Mass spectra were recorded with a LKB 9000 instrument with the settings: ion source temperature 270°C, accelerating voltage —3.5 kV and electron energy 70 eV.

Analyses were performed by A. Bernhard, 5251 Elbach, W.-Germany. Melting points are uncorrected.

Preparation of (R or S)-carvonerhodium(I) chloride (I)

A. From $RhCl_3 \cdot 3H_2O$

600 mg (4 mmole) (R or S)-carvone and 530 mg (2 mmole) $RhCl_3 \cdot 3H_2O$ are dissolved in 30 ml 95% ethanol and the mixture is refluxed for 2 h. The clear red solution is poured into a mixture of 100 ml $CHCl_3$ and 100 ml H_2O. The organic layer is separated after shaking, washed with 50 ml H_2O, dried with Na_2SO_4 and then filtered. The solution is concentrated to 15 ml in vacuo. 75 ml n-hexane is added and the mixture stored 2 h at room temperature and 8 h in the refrigerator. The brown crystalline precipitate is separated and purified twice by differential solvent ($CHCl_3$/n-hexane) crystallization. Yield 565 mg (87%), yellow-brown crystals.

[(R)-carvonerhodium(I) chloride]$_2 \cdot$2HCl. M.p. 210°C (dec.); $[\alpha]_D^{20}$ + 470° (c 0.1 $CHCl_3$). Found: C, 37.28; H, 4.36; Cl, 22.23; mol.wt. 702 (osmometric in $CHCl_3$). $C_{20}H_{30}Cl_4O_2Rh_2$ calcd.: C, 36.95; H, 4.65; Cl, 21.81%; mol.wt. 650.1 (mol.wt. 576 (mass spectr.), $C_{20}H_{28}Cl_2O_2Rh_2$ calcd.: 577.13).

[(S)-carvonerhodium(I) chloride]$_2 \cdot$2HCl. M.p. 210°C (dec.); $[\alpha]_D^{20}$ — 435° (c 0.1 $CHCl_3$). Found: C, 36.74; H, 4.39%. IR absorption spectra: 2970 m, 2880 s, 1665 vs, 1500 w, 1465 w, 1430 m, 1410 w, 1370 m, 1350 m, 1315 s, 1133 m, 1103 m, 1043 s, 1033 s, 1023 s, 998 m, 963 m, 928 w, 850 m, 750 vs (in KBr).

B. By olefin exchange

389 mg (1 mmole) $(C_2H_4)_4Rh_2Cl_2$ [4] is dissolved in 15 ml chloroform and 600 mg (4 mmole) (R)-carvone is added. Ethene is evolved and selectively identified by GLC [13]. The mixture is filtered after stirring for 3 h. 75 ml n-hexane is added and the mixture is stored for 10 h in the refrigerator. Work-up as under A. Yield 510 mg (78%).

[(R)-carvonerhodium(I) chloride]$_2 \cdot$2HCl. M.p. 210°C (dec.); $[\alpha]_D^{20}$ + 460° (c 0.1 $CHCl_3$). Found: C, 36.86; H, 4.25%; mol.wt. 748 (osmometric in $CHCl_3$); 576 (mass spectr.). IR absorption spectra as under A.

Diolefin displacement

A. By cyanide

Displacement of the dienone by cyanide is carried out according to ref. 6.

Unchanged carvone is identified by the combination GLC—MS and compared with an authentic sample. $[\alpha]_D^{20}$ + 56° (c ~ 0.3 $CHCl_3$), when obtained from [(S)-carvonerhodium(I) chloride]$_2$·2HCl ($[\alpha]_D^{20}$ — 435°).

B. By cycloocta-1,5-diene (COD)

65 mg (0.1 mmole) (I) is dissolved in 30 ml ethanol and 100 µl COD is added. The mixture is stirred for 30 min, then 25 ml ethanol is removed in vacuo. Yellow crystals of $[(COD)RhCl]_2$ separate. The IR spectrum is identical with that of an authentic sample of $[(CODRhCl]_2$ [1]. The presence of free carvone is recognized by its typical odour.

Preparation of (S)-carvonerhodium(I) acetylacetonate (II).

28 mg (0.22 mmole) sodium acetylacetonate (obtained from acetylacetone and sodium in benzene) is dissolved in 95% ethanol and the solution of 65 mg (0.1 mmole) (I) containing (S)-carvone in 10 ml 95% ethanol is added. The mixture is stirred for 10 min and the solvent then removed in vacuo. The residue is extracted with chloroform. The solution is filtered, concentrated, and chromatographed on inactive alumina with chloroform. The solvent is removed in vacuo and the orange product sublimed twice at 100°C/5·10^{-3} mm Hg. Yield 65 mg (92%). M.p. 117°C; $[\alpha]_D^{20}$ + 135° (c 0.05 $CHCl_3$). Found: C, 51.90; H, 5.99; mol. wt. 352 (mass spectr.). $C_{15}H_{21}O_3Rh$ calcd.: C, 51.15; H, 6.01%; mol.wt. 352.22. IR absorption spectrum: 2880 s, 2820 m, 1660 vs, 1560 s, 1515 s, 1462 w, 1424 w, 1386 m, 1364 m, 1316 w, 1270 m, 1028 m, 797 m, 743 w, (in KBr).

Preparation of (R)-carvonerhodium(I) h^5-cyclopentadienide (III)

125 µl by thermal degradation of dicyclopentadiene obtained cyclopentadiene is treated with 16 mg sodium dispersion in 25 ml dry tetrahydrofuran under nitrogen. Excess of cyclopentadiene is removed in vacuo, and then 65 mg (0.1 mmole) (I) containing (R)-carvone dissolved in 15 ml tetrahydrofuran is added. The mixture is stirred for 30 min and the solvent then removed in vacuo. The residue is extracted with n-hexane. n-Hexane is removed in vacuo and the residue is chromatographed on inactive alumina with chloroform. The product is sublimed at 100°C/5·10^{-3} mm Hg. Yield 54 mg (85%). Red needles are obtained by recrystallization from n-hexane. M.p. 176°C; $[\alpha]_D^{20}$ —141° (c 0.5 $CHCl_3$). Found: C, 56.93; H, 6.08; mol.wt. 318 (mass spectr.). $C_{15}H_{19}ORh$ calcd.: C, 56.62; H, 6.02%; mol.wt. 318.22.

Preparation of (S)-carvonerhodium(I) 3-trifluoroacetyl-(1R)-camphorate (IVa)

65 mg (0.1 mmole) (I) containing (S)-carvone, dissolved in 10 ml 95% ethanol, is added to the solution of 69 mg (0.11 mmole) barium(II) bis(3-trifluoroacetyl-(1R)-camphorate) [11] in 10 ml ethanol. After 10 min stirring at 50°C, the solvent is removed in vacuo. The residue is extracted with chloroform. The solution is filtered, concentrated and chromatographed on inactive alumina with chloroform. The solvent is removed in vacuo and the residue is sublimed at 140°C/5·10^{-3} mm Hg. Yield 93 mg (93%). M.p. 177°C; $[\alpha]_D^{20}$ +200° (c 0.05 $CHCl_3$). Found: C, 53.23; H, 5.65; mol.wt. 500 (mass spectr.). $C_{22}H_{28}F_3O_3Rh$ calcd.: C, 52.81; H, 5.64%; mol.wt. 500.35.

Preparation of (R)-carvonerhodium(I) 3-trifluoroacetyl-(1R)-camphorate (IVb)

A. From $RhCl_3 \cdot 3H_2O$, without isolation of (I)

300 mg (2 mmole) (*R*)-carvone and 265 mg (1 mmole) $RhCl_3 \cdot 3H_2O$ are dissolved in 25 ml 95% ethanol and refluxed for 2 h. To this solution is then added 316 mg (0.5 mmole) barium(II) bis(3-trifluoroacetyl-(1*R*)-camphorate) [11] dissolved in 30 ml ethanol. $BaCl_2$ precipitates immediately. After 10 min refluxing the solution is filtered and ethanol is removed in vacuo. Work-up as for (IVa). Yield 430 mg (86%). M.p. 209°C; $[\alpha]_D^{20}$ $-37°$ (*c* 0.05 $CHCl_3$). Found: C, 53.03; H, 5.8; mol.wt. 500 (mass spectr.).

B. By olefin exchange

41 mg (0.1 mmole) Diethylenerhodium(I) 3-trifluoroacetyl (1*R*)-camphorate [11] is dissolved in 5 ml chloroform and 15 mg (0.1 mmole) (*R*)-carvone added via a 25 μl syringe. Ethene is evolved and is identified selectively by GLC [13]. After stirring for 2 h the solvent is allowed to evaporate slowly at 20°C. The yellow crystals formed are collected and washed with cold n-pentane. M.p. 209°C. Found: C, 53.47; H, 5.79%; mol.wt. 500 (mass spectr.).

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