Rhodium(I)-centered cyclotriveratrylene


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Abstract. The rigid bowl-shaped molecule cyclotriveratrylene (CTV,1) was provided with short and long spacer arms terminating in triphenyl phosphite functions. These CTV ligands were used to immobilize a rhodium(I)-carbonyl-hydride complex. The ligand with short spacers gave a rigid, strained complex with a trigonal-coordination sphere around the rhodium. The ligand with long flexible spacers allowed the formation of a large cavity after the complexation to the rhodium center. This cavity, however, is filled up by the spacer arms, as was indicated by NMR studies. Variable-temperature NMR experiments suggested that the H-Rh-CO dipole in the rhodium-CTV complex can adopt two orientations: one with the hydride group pointing away from the CTV cavity (low-temperature conformation) and one in which this orientation is inverted (high-temperature conformation).

Introduction

Concave molecules are currently receiving interest as construction units for molecular and supramolecular architectures with unique properties. These molecules may also serve as a starting point for rigid ligand systems with specific bite angles, which maintain a certain coordination sphere around a metal center. Such a fixed-coordination environment can influence the properties of the remaining ligands on the metal and hence the catalytic activity of the complex. Concave molecules can furthermore function as a base for the construction of larger molecular systems with distinct cavities or clefts. Combining these systems with a catalytically active center is of great interest for the development of synthetic systems that mimic enzymatic activity.

Cyclotriveratrylene (1, CTV) is a bowl-shaped molecule, which has a rigid conformation as a result of restricted pseudo-rotation around the methylene groups in its nine-membered ring. CTV has been provided with long chains and crown ethers, and has been coupled to cyclotriguaiacylene (4) with K2CO3 in acetone, to give compound 5 in 28% yield. Deprotection of the hydroxyl group yielded the trihydroxy compound 6 (33%). After reacting 6 with diphenyl phosphochloridite and Et3N in CH2Cl2 compound 2 was obtained (76%).

Synthesis

The synthetic routes to ligands 2 and 3 are depicted in Schemes 1 and 2, respectively. In 2, the phosphate ligands are linked to the CTV unit by a short methylene spacer. In 3, the connection is achieved with a long and more flexible 3-CH2-C6H4-CH2-O group. For ligand system 2, the phenolic hydroxyl group of 4-hydroxybenzyl alcohol was first protected with an allyl function, after which the benzylic alcohol group was quantitatively converted into a benzylic chloride with thionyl chloride. This product was coupled to cyclotriguaiacylene (4) with K2CO3 in acetone, to give compound 5 in 28% yield. Deprotection of the hydroxyl group yielded the trihydroxy compound 6 (33%). After reacting 6 with diphenyl phosphochloridite and Et3N in CH2Cl2 compound 2 was obtained (76%). Compounds 5 and 6 appeared to be unstable due to the acid lability of the benzyl-aryl-ether moieties, which were readily hydrolyzed. The relatively low yield of 5 and 6 is the result of hydrolysis during the column-chromato-
graphic purification of these compounds on silica. Other purification methods were investigated but failed.

Compound 3 was built up from 4 directly (Scheme 2). Reaction of the latter compound with an excess of 1,3-bis(bromomethyl)benzene in acetone with K₂CO₃ as a base gave the tris(benzyl bromide) 7 (38%). Under the same conditions benzene-1,4-diol was coupled to 7 leading to the trishydroxy compound 8 in 47% yield. Reaction of the latter product with diphenyl phosphochloridite and Et₃N in dichloromethane gave ligand system 3 (79%). Compounds 2 and 3 were fully characterized (see Experimental section).

**Rhodium(I) complexes**

The rhodium complexes 9 and 10 were prepared by addition of an equimolar amount of (acac)Rh(CO)₂ (Hacac = acetylacetone = pentane-2,4-dione) to a solution of the corresponding ligands in chloroform and subsequent stirring for 10 hours under an H₂/CO atmosphere [P(H₂/CO) = 10 atm, H₂/CO = 3/1 v/v]. Isolation of the complexes was possible by precipitation in hexane, but was accompanied by partial loss of CO (approximately 20%). As a result no reproducible elemental analyses could be obtained. However, when the precipitates were redissolved and CO was bubbled through the solutions, complexes with the same properties as before were again formed. The spectroscopic properties of the complexes are summarized in Table I. For comparison, data for the reference compound HRhCO[P(OOPh)]₃ are also included in this table. The Rh center in this complex has a trigonal bipyramidal coordination sphere, with the phosphite ligands lying in the equatorial plane. The ³¹P-NMR spectrum of HRhCO[P(OOPh)]₃ in CDCl₃ displays a single doublet at δ 138.7 (Jₐₐ = 239 Hz). In the high-field region of the ¹H-NMR spectrum, hydride signal in the form of a doublet at δ ~ 10.59 (Jₐₐ = 3 Hz) is present, indicating that the cis-P-H couplings are very small. The ³¹P(¹H)-NMR spectrum of complex 9 in CDCl₃ (Figure 1a) is similar to that of HRhCO[P(OOPh)]₃ and shows a single, broadened doublet. The signal of the hydride in the high-field region of the ¹H-NMR spectrum is also broadened (Figure 1b). This broadening can be explained by the fact that the spacers in 9 are short, which prevents the phosphite ligands adopting a purely planar arrangement around the Rh atom. Since the ligands are slightly pulled out of the trigonal plane, some P-H coupling occurs. This distortion of the trigonal bipyramidal conformation is also expressed by the weakening of the Rh-H bond (IR: ν 2001 cm⁻¹). The similarities

<table>
<thead>
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<th>Table I Spectroscopic data of the rhodium complexes.</th>
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<tr>
<td>³¹P-NMR b δ (ppm), [Jₐₐ, (Hz)]:</td>
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<td>¹H-NMR c δ (ppm), [Jₐₐ, (Hz)]:</td>
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<td>¹³Rh-NMR c δ (ppm), [Jₐₐ, (Hz)]:</td>
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<td>IR c ν [Rh-CO (cm⁻¹)]:</td>
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<td>ν [Rh-H (cm⁻¹)]:</td>
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a At 298K, in CDCl₃, referenced to external OP(OMe). b At 298K, in CDCl₃, referenced to TMS. c In KBr.
The 31P{1H} NMR spectrum of the rhodium-carbonyl-hydride complex of 3 in CDCl3 displays a set of resonances, in which the intensity ratio changes with concentration (Figure 2). At low concentrations (approximately 0.5 mM), only doublets at 140.0 ppm and 140.2 ppm remain, which we attribute to complex 10. In 10, the spacer groups are sufficiently long to allow a crossed arrangement of the chains connecting the rhodium center and the CTV unit. Space-filling models show that an excellent fit of the spacer parts is possible in this folded conformation. The twist induces an additional dyssymmetry in the molecule. As we started from a racemic mixture of CTV molecules, the formation of 10 leads to two pairs of enantiomers (10a and 10b, see Figure 3) and, as a result, to two doublets in the 31P-NMR spectrum. Another indication of the occurrence of diastereomers is found in the 1H-NMR spectrum of the complex, i.e., an asymmetric pattern for the signal of the methoxy groups and complex signals for the benzylic protons.

In more concentrated solutions (2 mM, see Figure 2c) a broad band at 139.5 ppm dominates the 31P-NMR spectrum, accompanied by a sharp doublet at 139.7 ppm. The broad band probably originates from a polymeric form, as proposed in Figure 4a. The sharp additional signal possibly comes from a specific oligomeric species, e.g., a dimeric complex (Figure 4b).

To support the existence of two diastereomers of complex 10 we carried out 103Rh-NMR measurements. The data were obtained by REVERSE 2D, 1H-103Rh spectroscopy. The concentration was such that only compound 10 was present (ca. 0.4 mM). The 103Rh-NMR spectrum of the reference compound HRhCO[P(OPh)3] showed a quartet at δ = -1258 (J_Rh-P 239 Hz). The 1H-103Rh 2D spectrum of 10 revealed two partially overlapping quartets for the Rh-signal (Figure 5, outer parts not shown), indicating the presence of two different complexes. The distribution of the intensity of the cross peaks possibly implies that the signs of the Rh–H couplings in the two pairs of enantiomers are opposite. As the signal pattern in the 31P-NMR spectrum is very simple (vide supra), the splitting of the Rh signal cannot be a consequence of an additional Rh–P coupling due to the inequivalence of the phosphorus atoms in the twisted molecules. Moreover, the Rh–P coupling constants of the two diastereomers 10a and 10b are slightly, but significantly different (Table 1). The energy of activation required to interconvert the two twisted forms of 10 is expected to be considerable because an extensive conformational change is required, as shown by CPK models.
Variable-temperature NMR experiments

The $^{31}$P-NMR signals of both 9 and 10 shift when the temperature is varied (Figure 6), suggesting that in solution two additional forms of complexes exist which are in rapid equilibrium. One form, characterized by $\delta_{\text{max}}$, is in excess at low temperature while the other ($\delta_{\text{min}}$) is dominant at high temperature. We propose that these two forms differ in the way the H–Rh–CO dipole is oriented with respect to the CTV framework (shown for 10 in Figure 7). Both the metal complex part and the CTV unit are strongly polarized. Consequently, their dipoles can align or oppose. The equilibrium constant for the process of interconversion at a certain temperature is given by the expression:

$$K_{\text{eq}} = \frac{\delta_{\text{obs}} - \delta_{\text{min}}}{\delta_{\text{max}} - \delta_{\text{obs}}}$$

Evaluation of the temperature dependence of this equilibrium constant by fitting the data to the Arrhenius equation, yielded the thermodynamic parameters listed in Table II. We explain these results as follows. At low temperatures the dipoles of the CTV unit and the Rh complex align, with the hydride ligand pointing away from the cavity (Figure 7). The total dipole moment causes a high degree of organization of the solvent molecules ($\mu$ (CHCl$_3$) 1.05 D). At high temperatures, the H–Rh–CO dipole inverts, the total dipole moment becomes smaller, and, as a result, solvent molecules are released, explaining the high positive value of $\Delta S$. To check this explanation we determined the dipole moments of HRh[PO(OH)$_2$]$_3$ and CTV (1) separately. They amounted to 2.42 (±0.12) D (tetrachloromethane) and 2.80 (±0.20) D (benzene), respectively. The dipole moment of 1 was also calculated, giving $\mu = 3.2$ D. The fact that the experimentally determined value is smaller than the calculated one may be ascribed to interactions with the benzene solvent molecules.

Complexation experiments

It is known that cryptophanes can strongly bind tetrahedral substrates such as chloroform, isobutane and tetramethylammonium ions. The binding is explained in terms of Van der Waals interactions and cation–π interactions.

Despite the structural analogy between the larger cryptophane-E and complex 9 no binding of chloroform or toluene molecules was observed by the latter compound, as confirmed by NMR experiments. Nor was any binding observed with complex 10. Apparently, the energy barrier to untwist the folded conformation of this metallohost to produce an open cavity is too high.

Conclusions

We have shown that CTV can act as a template to construct rigid chelating ligand systems with a trigonal coordination symmetry. The complex prepared from the ligand system with long flexible spacers does not bind substrate molecules, probably because it is entropically more favorable to fill up the cavity by twisting the spacer arms. The fixation of two relatively strong dipolar moieties in close proximity to one another as in 9 and 10 gives rise to molecules with interesting conformational properties.

Experimental section

General

Unless indicated otherwise, commercial materials were used as received. Hexane and toluene were distilled under nitrogen atmosphere from sodium. Dichloromethane and tetrahydrofuran were distilled from LiAlH$_4$, chloroform and chloroform-d$_4$ were distilled from phosphorus pentoxide. All solvents were stored on molecular sieves under an inert atmosphere. $^1$H-NMR spectra were recorded on Bruker WH-90, Bruker AC-100, Bruker WM-200 and Bruker AM-400 instruments. Chemical shifts (δ) are reported in ppm downfield from internal (CH$_3$)$_2$Si. Abbreviations used are s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and br = broad.

Rh-NMR spectra were recorded on Bruker WH-90, Bruker AC-100, Bruker WM-200 and Bruker AM-400 instruments. Chemical shifts (δ) are reported in ppm downfield from external OP(OMe)$_3$. The WM-200 apparatus was calibrated for the temperature with methanol according the protocol of van Geetx. The $^{31}$P-NMR spectra were recorded on a Bruker AC-100 instrument with ‘reverse’ modification. Chemical shifts are reported in ppm relative to $^3$P, 8.0 MHz, negative values to low frequency. FAB mass spectra were recorded on a VG 7070E instrument, the matrix used was 3-nitrobenzyl alcohol. Elemental analyses were determined with a Carlo Erba EA 1108 instrument. Dipole moments were determined on a WTW Dipolimeter, type DM 01. IR spectra were recorded on a Perkin Elmer IR/FT spectrometer 1720X. For column chromatography Merck silica gel (60H) was used and for thin layer chromatography Merck silica gel 60 F$_{254}$ plates were employed.

Cyclotrimerene (1)

This compound was synthesized according to a literature procedure. 4-Allyloxybenzyl alcohol

A mixture of 6 g (0.05 mol) of 4-hydroxybenzyl alcohol, 9 ml (0.11 mol) of allyl bromide and 12 g of K$_2$CO$_3$ in 300 ml of acetonitrile was...
The organic layer was washed with an 0.5N aqueous NaOH solution and evaporated to dryness under reduced pressure. Yield 7.8 g (98%) of product as a light yellow oil. 1H-NMR (90 MHz, CDCl₃): δ: 7.30 (d, 2H, ArH, J 6 Hz), 6.68 (d, 2H, ArH, J 8 Hz), 6.33-5.84 (m, 1H, OCH₂CH=CH₂), 5.55-5.17 (m, 2H, OCH₂CH=CH₂), 4.57 (s, 2H, CH₂Ar, J 6 Hz), 4.60-4.44 (m, 2H, OCH₂CH=CH₂). 10.15-Dihydro-2,1,12-trimethoxy-3,8,13-tris[3-(4-hydroxyphenoxy)methyl]benzyl-5H-tribenzo[a,d,g]cyclonene (race-7)

A solution of 1.6 g (3.9 mmol) of cyclotriguaiacylene (4), 2.8 g (15.3 mmol) of 4-Allyloxybenzyl chloride, and evaporated to dryness. The resulting oil was purified by column chromatography (silica, eluent: CHCl₃/MeOH 7,95/0.5 v/v) to yield 0.41 g (47%) of compound 2 using 0.2 g (0.19 mmol) of rac-3 and subsequently extracted with CHCl₃. The organic layer was washed with water (2x), dried (MgSO₄), and evaporated to dryness. The crude product was purified by column chromatography (silica, eluent: CHCl₃/MeOH 95/5 v/v) to yield 0.39 g (79%) of compound 3 as a white foam. 1H-NMR (200 MHz, CDCl₃): δ: 7.46–6.66 (m, 6H, ArH, J 8 Hz), 5.09 (s, 3H, CH₂OAr), 4.99 (s, 3H, CH₂OAr), 3.40 (s, 9H, OCH₃), 3.40 (s, 9H, OCH₃). 10.15-Dihydro-2,1,12-trimethoxy-3,8,13-tris[3-(4-hydroxyphenoxy)methyl]benzyl-5H-tribenzo[a,d,g]cyclonene (race-9)

A solution of 121 mg (81 µmol) of rac-3 and subsequently extracted with CHCl₃. The reaction mixture was concentrated to 2 ml and slowly added to 20 ml of hexane. The resulting precipitate was filtered off yielding 75 mg of a yellowish powder. 1H-NMR (200 MHz, CDCl₃): δ: 7.5–6.3 (m, br, 48H, ArH), 5.4–4.5 (br, 9H, ArCH₂, H₂OCH), 3.9–3.1 (br, 12H, OCH₃, CH₃OCH), -10.59 (d, 1H, Rh-H). 1P-NMR (80 MHz, CDCl₃): δ: 138.6 (d, J_Rh,P 239 Hz). No satisfying elemental analysis could be obtained for this product (see text).

Complex 10

Under an inert atmosphere, 0.3 ml (1.3 mmol) of dipherin phosphochloridite was added to a solution of 126 mg (0.07 mmol) of 6 and 0.2 ml (1.3 mmol) of triethylamine in 10 ml of CHCl₃. The mixture was refluxed for 1 h, after which its volume was reduced to 2 ml. This concentrated mixture was added to 25 ml of dry hexane. This resulted in a precipitate which was filtered off, washed with hexane, and subsequently extracted with CHCl₃. This solution was then evaporated under reduced pressure. Yield 0.26 g of a white crystalsine solid: 1H-NMR (90 MHz, CDCl₃): δ: 7.12 (d, 6H, ArH, J 8 Hz), 6.90 (s, 3H, ArHCTV), 6.88 (d, 6H, ArH, J 8 Hz), 6.60 (s, 3H, ArHCTV), 5.02 (s, 6H, ArCH₂), 4.76 (d, 3H, H₂OCH, J 14 Hz), 4.52–4.20 (b, 3H, CH₂, J 5 Hz), 3.75 (s, 9H, OCH₃), 3.49 (d, 3H, H₂OCH, J 14 Hz).

10.15-Dihydro-2,7,12-trimethoxy-3,8,13-tris[3-(4-hydroxyphenoxy)methyl]benzyl-5H-tribenzo[a,d,g]cyclonene (race-2)

The spectra were recorded on a Bruker AC100 spectrometer equipped with a 10-mm 10Rh-[31P, 1H] probe, a second PTS 160
synthesizer provided with a 90° phase shifter, a B-SV 3 heteronucleus decoupling unit with a selective \(^{103}\)Rh amplifier, and a B-VT 1000 temperature control unit (±1°C). The \(^{103}\)Rh-NMR signals were obtained indirectly by using the 2-D REVERSE-INEPT technique, giving the \(\delta^{(1)}\)Rh chemical shift and the coupling constant to phosphorus in the F1 dimension and the \(J_{\text{Rh-H}}\) in the F2 dimension.

**Dipole moment measurements**

Dipole moments were determined by measuring the dielectric constant and refractive index of a series of diluted solutions containing varying concentrations of CTV or complex. From these data the dipole moment could be obtained following the procedure of Guggenheim and Smith. The dipole moment of HRh(CO)\(_3\)[P(OPh)]\(_3\) was determined in tetrachloromethane and that of CTV in benzene.

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3k A very small \(cis-P-H\) coupling has also been observed in the case of HRh(CO)\(_3\)[P(o-C\(_6\)H\(_4\)-2-CMe\(_3\)]\(_3\);
3o N.F. Ramsey, Phys. Rev. 86, 243 (1952). It was found that the \(^{31}\)P NMR signal of HRhCO[P(OPh)]\(_3\) did not shift when the temperature was varied.
3p The dipole moments were evaluated from the point charges obtained by minimizing the electron distribution density using the MINDO/3 Hamiltonian and ESP electrostatic potential calculation (MOPAC Version 5.0).