Rhodium(I)-centered cyclotrimeratrylene

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Abstract. The rigid bowl-shaped molecule cyclotrimeratrylene (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-temper-
ature conformation).

Introduction

Concave molecules are currently receiving interest as construction units for molecular and supramolecular architec-
tures with unique properties.1 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.

Cyclotrimeratrylene (I, CTV) a 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.2 CTV has been provided with long
chains3a,b and crown ethers3c, and has been coupled to a
triaza-crown ether3d,e and a diphenylglycoluril unit3f.
Collet et al.2,4 have linked two CTV units in such a way
that the concave sides of these molecules face one an-
other, resulting in a new class of compounds, the so-called
"cryptophanes".

In this paper we present two new ligand systems (2 and 3),
which are derived from a CTV unit to which three triph-
enyl phosphite ligands have been attached. Ligand 2 has
short spacers between the CTV unit and the phosphite
groups, and is designed for binding a metal in such a way
that the phosphite groups are forced to adapt equatorial
positions at the metal center. The other ligand, 3, has long
flexible spacers allowing the formation of a cavity after
coordination of the phosphites to the metal center. Lig-
ands 2 and 3 have been used to synthesize rhodium(I)
complexes. The properties of these complexes are des-
cribed.

Results and discussion

Synthesis

The synthetic routes to ligands 2 and 3 are depicted in
Schemes 1 and 2, respectively. In 2, the phosphite 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 cyclotrimeratrylene5 (4) with K2CO3 in ace-
tone, to give compound 5 in 28% yield. Deprotection of
the hydroxyl group yielded the trihydroxy complex 6
(33%). After reacting 6 with diphenyl phosphorochloride
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 K\textsubscript{2}CO\textsubscript{3} 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 Et\textsubscript{3}N 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)\textsubscript{2} (Hacac = acetylacetone = pentane-2,4-dione) to a solution of the corresponding ligands in chloroform and subsequent stirring for 10 hours under an H\textsubscript{2}/CO atmosphere [P(H\textsubscript{2}/CO) = 10 atm., H\textsubscript{2}/CO = 3/1 \text{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[PO(PPh\textsubscript{3})\textsubscript{3}] are also included in this table\textsuperscript{6}. The Rh center in this complex has a trigonal bipyramidal coordination sphere, with the phosphite ligands lying in the equatorial plane. The \textsuperscript{31}P-NMR spectrum of HRhCO[PO(PPh\textsubscript{3})\textsubscript{3}] in CDCl\textsubscript{3} displays a single doublet at δ 138.7 (J\textsubscript{Rh-P} 239 Hz). In the high-field region of the \textsuperscript{1}H-NMR spectrum, hydride signal in the form of a doublet at δ -10.59 (J\textsubscript{Rh-H} 3 Hz) is present, indicating that the cis-P-H couplings are very small\textsuperscript{7}. The \textsuperscript{31}P(\textsuperscript{1}H)-NMR spectrum of complex 9 in CDCl\textsubscript{3} (Figure 1a) is similar to that of HRhCO[PO(PPh\textsubscript{3})\textsubscript{3}] and shows a single, broadened doublet. The signal of the hydride in the high-field region of the \textsuperscript{1}H-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\textsuperscript{6}. This distortion of the trigonal bipyramidal conformation is also expressed by the weakening of the Rh-H bond (IR: ν 2001 cm\textsuperscript{-1}). The similarities

### Table I Spectroscopic data of the rhodium complexes.

<table>
<thead>
<tr>
<th></th>
<th>HRhCO[PO(PPh\textsubscript{3})\textsubscript{3}]</th>
<th>9</th>
<th>10</th>
</tr>
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<tr>
<td>\textsuperscript{31}P NMR \textsuperscript{b}</td>
<td>\textsuperscript{1}H NMR \textsuperscript{c}</td>
<td>\textsuperscript{103}Rh NMR \textsuperscript{d}</td>
<td>IR \textsuperscript{e}</td>
</tr>
<tr>
<td>δ (ppm), [J\textsubscript{Rh-P}, (Hz)]</td>
<td>138.7 [239]</td>
<td>138.6 [239]</td>
<td>a: 140.2 [238]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>b: 140.0 [239]</td>
</tr>
<tr>
<td>δ (ppm), [J\textsubscript{Rh-P}, (Hz)]</td>
<td>-1258 [239]</td>
<td></td>
<td>a: -1262 [238]</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>b: -1259 [239]</td>
</tr>
<tr>
<td>ν [Rh-CO (cm\textsuperscript{-1})]</td>
<td>2050</td>
<td>2051</td>
<td>2050</td>
</tr>
<tr>
<td>ν [Rh-H (cm\textsuperscript{-1})]</td>
<td>1980</td>
<td></td>
<td>1984</td>
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between the spectra, however, indicates that 9 and the reference compound have similar geometries. The $^{31}$P–$^1$H–NMR spectrum of the rhodium–carbonyl–hydride complex of 3 in CDCl$_3$ 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 b, see Figure 3) and, as a result, to two doublets in the $^{31}$P–NMR spectrum. Another indication of the occurrence of diastereomers is found in the $^1$H–NMR spectrum of the complex, viz. an asymmetric pattern for the signal of the methoxy groups and complex signals for the benzyl protons.

In more concentrated solutions (2 mM, see Figure 2c) a broad band at 139.5 ppm dominates the $^{31}$P–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 $^{103}$Rh–NMR measurements. The data were obtained by REVERSE 2D, $^1$H–$^{103}$Rh spectroscopy. The concentration was such that only compound 10 was present (ca. 0.4 mM). The $^{103}$Rh–NMR spectrum of the reference compound HRhCO[P(OPh)$_3$]$_3$ showed a quartet at $\delta = 1258$ (J$_{Rh-P}$ 239 Hz). The $^1$H–$^{103}$Rh 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 $^{31}$P–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 I). 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 H RhCO[P(O)Ph]$_3$, 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.$^{11}$

**Figure 6.** Temperature dependence of the $^{31}$P NMR signals of complexes 9 and 10. The filled circles (Σ) are the experimental data points, the lines are obtained by calculation.

**Figure 7.** Schematic representation of the orientations of the dipoles originating from the metal complex part and the CTV subunit in compound 10.

### Table II

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\Delta G$ (kJ mol$^{-1}$, at 298 K)</th>
<th>$\Delta H$ (kJ mol$^{-1}$)</th>
<th>$\Delta S$ (J mol$^{-1}$ K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>–0.5</td>
<td>32.6</td>
<td>111</td>
</tr>
<tr>
<td>10a</td>
<td>–0.6</td>
<td>42.7</td>
<td>145</td>
</tr>
<tr>
<td>10b</td>
<td>–0.5</td>
<td>47.6</td>
<td>161</td>
</tr>
</tbody>
</table>

Complexation experiments

It is known that cryptophanes can strongly bind tetrahedral substrates such as chloroform, isobutane and tetramethylammonium ions.$^5$ The binding is explained in terms of Van der Waals interactions and cation–π interactions.$^{6,12}$ Despite the structural analogy between the larger cryptophane-E$^1$ 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.$^3$ $^1$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$_3$)$_3$Si. Abbreviations used are s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and br = broad.$^3$P–NMR spectra were recorded on Bruker WH-90 and Bruker AM-400 instruments. Chemical shifts (δ) are reported in ppm downfield from external OP(O)Me$_3$. The WM-200 apparatus was calibrated for the temperature with methanol according the protocol of van Geert.$^{13}$ The $^{110}$Rh–NMR spectra were recorded on a Bruker AC-100 instrument with ‘reverse’ modification. Chemical shifts are reported in ppm relative to $^2$H$_2$O, 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 Dipolmeter, type DM 01. IR spectra were recorded on a Perkin Elmer IR FT spectrometer 1720 X. For column chromatography Merck silica gel (60 H) was used and for thin layer chromatography Merck silica gel 60 F$_254$ plates were employed.

**Cyclotriveratrylene (1)**

This compound was synthesized according to a literature procedure.$^{11}$

**4-Alllyloxybenzyl 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 acetone was
refluxed overnight. The solvent was removed under reduced pressure. The residue was added, and the product was extracted with CH₂Cl₂. The organic layer was washed with an 0.5N aqueous NaOH solution (2 × 1), with water (2 ×), dried (MgSO₄) 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 8 Hz), 6.88 (d, 2H, ArH, J 8 Hz), 6.33-5.84 (m, 3H, OCH₃-CH =, 3.64 (s, 2H, CH₂Ar), 4.46 (m, 1H, OCH₂CH₂), 1.64 (dd, 1H, HO-CH₂-Ar) J 5 Hz and J 6.4 Hz). The crude product was used without further purification.

4-Allyloxybenzyl chloride

To a cooled solution (0°C) of 2.5 g (15 mmol) of 4-allyloxybenzyl alcohol in 125 mL of dichloromethane was added over a period of 30 min 2.5 g (21 mmol) of thionyl chloride, and evaporated to dryness in 125 mL of dichloromethane. The mixture was subsequently stirred at room temperature for 1 h and evaporated to dryness under reduced pressure giving 2.7 g (100%) of 4-allyloxybenzyl chloride as a yellow oil. ¹H-NMR (90 MHz, CDCl₃) δ: 7.32 (d, 2H, ArH, J 8 Hz), 6.68 (d, 2H, ArH, J 8 Hz), 6.33-5.84 (m, 1H, OCH₂CH₂ = CH₂), 5.55-5.17 (m, 1H, OCH₂H = CH₂), 4.57 (s, 2H, CH₂Ar), 4.60-4.44 (m, 2H, OCH₂CH₂ = CH₂).


A mixture of 1.6 g (3.9 mmol) of cyclotriguaiacylene (4), 2.8 g (15.3 mmol) of 4-allyloxybenzyl chloride, 2 g of potassium carbonate, and a catalytic amount of potassium iodide in 200 mL of acetone was refluxed for 18 h. The solvent was evaporated to dryness and 150 mL of hexane was added, and the resulting suspension was extracted with CH₂Cl₂ (2 ×). The organic layer was washed with water (2 ×), dried (MgSO₄), and evaporated to dryness. The resulting oil was purified by column chromatography (silica, eluent: CHCl₃), resulting in 0.92 g (28%) of the product. The product was purified by column chromatography (silica, eluent: CHCl₃/MeOH 95.5/0.5 v/v), yielding 75 mg of a yellowish powder. ¹H-NMR (200 MHz, CDCl₃) δ: 7.46-6.66 (m, 60H, ArH), 5.09 (s, 3H, CH₃-OAr), 4.72 (d, 3H, ArH, J 14 Hz), 3.64 (s, 3H, OCH₃), 3.44 (d, 3H, H₂O-CH₂), 1.46 (s, FAB-MS m/z: 1029 (M+H)+). Anal. calc. for C₄₂H₃₃O₃P₃: C 71.57, H 5.24; found: C 71.55, H 5.21%.

Complex 9

A solution of 112 mg (81 ¿¿mol) of 2 and 21 mg (81 ¿imol) of 12-trimethoxy-3,8,13-tris(13-1-[4-(diphenylphosphito)tribenzol[1,2-f:2',1'-d:5',1'-h]cyclononene (complex 9)

For the preparation of this complex, the same procedure was followed as described for compound 9 using 107 mg (63 ¿¿mol) of 3 and 16.3 mg (63 ¿¿mol) of (acac)RbHCO₃; yield 87 mg (75%) of a yellowish powder. ¹H-NMR (200 MHz, CDCl₃) δ: 7.5-6.6 (m, 60H, ArH), 5.09 (s, 3H, CH₃-OAr), 4.72 (d, 3H, ArH, J 14 Hz), 3.69 (s, 3H, OCH₃), 3.42 (d, 3H, H₂O-CH₂), J 14 Hz). FAB-MS m/z: 1259 (q, 1259). ³¹P-NMR (80 MHz, CDCl₃) δ: 138.6 (d, JPP= 239 Hz). No satisfying elemental analysis could be obtained for this product (see text).

Complex 10

The spectra were recorded on a Bruker AC100 spectrometer equipped with a 10-mm ¹³C- and ¹H probe, a second PTS 160
synthesizer provided with a 90° phase shifter, a B-SV 3 heteronu-
cleus decoupling unit with a selective $^{103}\text{Rh}$ amplifier, and a B-VT
1000 temperature control unit (±1°C). The $^{103}\text{Rh}$-NMR signals
were obtained indirectly by using the 2-D REVERSE-INEPT tech-
nique, giving the $\delta(^{1}H)$ and $J_{\text{Rh-H}}$ in the F2 dimension.

Dipole moment measurements

Dipole moments were determined by measuring the dielectric con-
stant 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.\(^5\) The dipole moment was first calibrated with
thoroughly purified cyclohexane, tetrachloromethane, benzene and
dibutyl ether.\(^6\) The dipole moment of HRh(CO)$_3$[P(OPh)$_3$]$_3$
was determined in tetrachloromethane and that of CTV in benzene.

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