Synthesis and Conformational Behavior of Rhodium(I) Metallohosts Derived from Diphenylglycoluril

Hein K. A. C. Coolen,[†] Piet W. N. M. van Leeuwen,[‡] and Roeland J. M. Nolte*[,†]

Department of Organic Chemistry, Nijmegen SON Research Center, Toernooiveld, 6525 ED Nijmegen, The Netherlands, and Department of Chemical Engineering, J. H. van't Hoff Instituut, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

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The design and synthesis of molecules containing both a substrate-binding cavity and a nearby catalytically active metal center is a useful approach to the development of synthetic systems that function according to the principles of enzymes. To this end the receptor molecule **2a**, derived from diphenylglycoluril, was functionalized with triaryl phosphite ligands to give the receptor ligand **2d**. Exchange reactions of **2d** with (diketonate)$Rh(CO)_2$, (diketone = acetylacetone, dibenzoylmethane, or dipivaloylmethane) led to the formation of the metallohosts **3a**−**c**, respectively. The properties and conformational behavior of these metal complexes were studied by NMR techniques. Reaction of compounds **3** with H_2 in the presence of a small excess of additional triphenyl phosphite yields the rhodium(I) hydride complex **5**. The metallohosts are capable of binding dihydroxybenzene guests in their cavities by hydrogen bonding and $\pi-\pi$ stacking interactions. On binding a substrate the conformational behavior of hosts **3a**−**c** was affected considerably.

Introduction

Current interest in the field of supramolecular chemistry is focused on the design of advanced molecular devices and catalytic systems. As a result of built-in ordering or information the system or device is intended to perform certain actions, mostly based on and inspired by biological processes. Macrocyclic rings and molecular cages have been synthesized and explored for applications such as selective recognition,[1] transport,[2] switching,[3] self-replication,[4] and catalysis.[1b,5] For a supramolecular catalyst, a host is required that recognizes the substrate selectively and contains a nearby catalytic center that can convert the bound substrate, and finally, the catalyst should be able to release the product and have the property to be regenerated efficiently. Our objective is to develop these systems by the design and synthesis of molecules containing both a cavity and a catalytically active metal center. Several examples of hosts[6] with metal centers have been described in the literature., *e.g.* functionalized cyclodextrines,[5a,7] capped porphyrins,[6,8] and modified cyclophanes.[1b]

In this paper we decribe host molecules that are provided with a nearby Rh(I)−triorganyl phosphite complex. They are synthesized from the clip molecule **1a**, which is derived from diphenylglycoluril.[9] These metallohosts are selective hydrogenation and isomerization catalysts for dihydroxy-substituted allylarene substrates, as will be described in a separate paper.[10]

Results and Discussion

Design. The substrate-binding moiety of our metallohosts is molecule **2a** (R = H), previously reported by us.[11] The central part of this molecule has the form of a clip (see Figure 1).[12] The two side walls of **1a** are connected by azatetrakis(ethylene glycol) chains, giving the molecule the structure of a basket. The nitrogen atoms in the rings can be used to functionalize the basket with metal binding ligands, *viz.* by connecting them *via* spacers. The form and the length of the spacers will define the final flexibility and property of the system. Since the rings of **2a** contain many hard donor atoms we decided to connect soft donor ligands to the nitrogen atoms in order to be able to distinguish between the two ligating moieties (Pearson's HSAB theorem[13]). The chelate effect is expected to be small because of the large

[†] Nijmegen SON Research Center.

[‡] J. H. van't Hoff Institute.

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(1) (a) Gokel, G. W. *Crown Ethers and Cryptands*; Royal Society of Chemistry: Cambridge, U.K., 1991. (b) Diederich, F. *Cyclophanes*; Royal Society of Chemistry: Cambridge, U.K., 1991. For other examples, see: (c) Fan, E.; Vanarman, S. A.; Kincaid, S. Hamilton, A. D. *J. Am. Chem. Soc.* **1993**, *115*, 369. (d) Yoon, S. S.; Still, W. C. *Ibid.* **1993**, *115*, 823. (d) Rebek, J., Jr.; Nemeth, D. *Ibid.* **1985**, *107*, 6738. (e) Schmitchen, F. P. *Tetrahedron Lett.* **1989**, *30*, 4493. (f) Dougherty, D. A.; Stauffer, D. A. *Science* **1990**, *250*, 1558.

(2) See for example: (a) Nijenhuis, W. F.; Buitenhuis, E. G.; de Jong, F.; Sudhölter, E. J. R.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1991**, *113*, 7963. (b) Pregel, M. J.; Jullien, L.; Lehn, J.-M. *Angew. Chem.* **1992**, *104*, 1695. (c) Roks, M. F. M.; Nolte, R. J. M. *Macromolecules* **1992**, *25*, 5398. (d) van Straaten-Nijenhuis, W. F.; van Doorn, A. R.; Reichwein, A. M.; de Jong, F.; Reinhoudt, D. N. *J. Org. Chem.* **1993**, *58*, 2265. (e) Rebek, J., Jr.; Askew, B.; Nemeth, D.; Parris, K. *J. Am. Chem. Soc.* **1987**, *109*, 2432.

(3) See for example: (a) Beer, P. D. *Chem. Soc. Rev.* **1989**, *18*, 409. (b) Shinkai, S. *Pure Appl. Chem.* **1987**, *59*, 425. (c) Sabbatini, N.; Guardigli, M.; Lehn, J.-M. *Coord. Chem. Rev.* **1993**, *123*, 201. (d) Cobben, P. L. H. M.; Egberink, R. J. M.; Bomer, J. G.; Bergveld, P.; Verboom, W.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1992**, *114*, 10573.

(4) (a) Nowick, J. S.; Feng, Q.; Tjivikua, T.; Ballester, P.; Rebek, J., Jr. *J. Am. Chem. Soc.* **1991**, *113*, 8831. (b) Park, T. K.; Feng, Q.; Rebek, J., Jr. *Ibid.* **1992**, *114*, 4529.

(5) See for example: (a) Tabushi, I. *Acc. Chem. Res.* **1982**, *15*, 66. (b) Anslyn, E.; Breslow, R. *J. Am. Chem. Soc.* **1989**, *111*, 8931. (c) Kelly, T. R.; Bridger, T. J.; Zhao, C *J. Am. Chem. Soc.* **1990**, *112*, 8024. (d) Walter, C. J.; Anderson, H. L.; Sanders, J. K. M. *J. Chem. Soc., Chem. Commun.* **1993**, 458.

(6) Meade T. J.; Busch, D. H. *Prog. Inorg. Chem.* **1985**, *33*, 59.

(7) (a) Breslow, R.; Overman, L. E. *J. Am. Chem. Soc.* **1970**, *92*, 1075. (b) Komiyama, M.; Matsumoto, Y. *Chem. Lett.* **1989**, 719.

(8) (a) Baldwin, J. E.; Perlmutter, P. *Top. Curr. Chem.* **1984**, *121*, 181. (b) Mansuy, D. *Pure Appl. Chem.* **1987**, *59*, 759. (c) Groves, J. T.; Viski, P. *J. Am. Chem. Soc.* **1989**, *111*, 8537; *J. Org. Chem.* **1990**, *55*, 3628. (d) Collman, J. P.; Zhang, X.; Lee, V. J.; Brauman, J. I. *J. Chem. Soc., Chem. Commun.* **1992**, 1647.

(9) Smeets, J. W. H.; Sijbesma, R. P.; Niele, F. G. M.; Spek, A. L.; Smeets, W. J. J.; Nolte, R. J. M. *J. Am. Chem. Soc.* **1987**, *109*, 928.

(10) Coolen, H. K. A. C.; Meeuwis, J. A. M.; van Leeuwen, P. W. N. M.; Nolte, R. J. M. *J. Am. Chem. Soc.* **1995**, *117*, 11906.

(11) (a) Smeets, J. W. H.; Sijbesma, R. P.; van Dalen, L.; Spek, A. L.; Smeets, W. J. J.; Nolte, R. J. M. *J. Org. Chem.* **1989**, *54*, 3710. (b) Smeets, J. W. H.; Visser, H. C.; Kaats-Richters, V. E. M.; Nolte, R. J. M. *Recl. Trav. Chim. Pays-Bas* **1990**, *109*, 147.

(12) Sijbesma, R. P.; Bosman, W. P.; Nolte, R. J. M. *J. Chem. Soc., Chem. Commun.* **1991**, 885.

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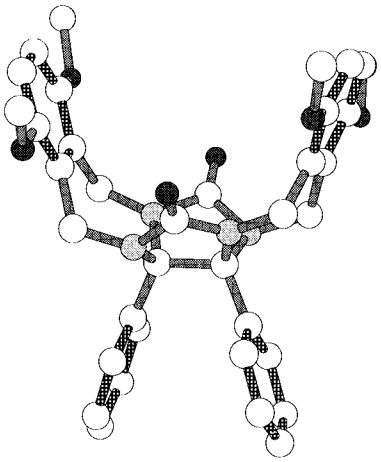


Figure 1. X-ray structure of **1a** (see ref 12).

distance between the two ligands of modified **2a**. In order to avoid displacement of the bound metal center by exchange with other ligands, the applied metal complex must not be kinetically too labile. The combination of rhodium(I) and triaryl phosphite ligands was felt to meet the above-mentioned criteria.

Synthesis. The synthesis of the ligand system is outlined in Scheme 1. The starting compound is tetrapodand **1b**.[14] Double ring closure of **1b** with 2 equiv of *p*-(methoxymethoxy)benzylamine under high dilution conditions in acetonitrile with Na_2CO_3 as a base gave **2b** (62% after column chromatography). The *p*-hydroxybenzylamine was prepared from cyanophenol according to a standard procedure (see the Experimental Section). Quantitative removal of the *p*-methoxymethyl groups of **2b** was achieved with concentrated hydrochloric acid to give **2c**·2HCl (Chart 1). This compound can be deprotonated with a $NaHCO_3$/NaOH buffer of pH = 9.8, albeit with loss of product. CPK models suggest that in deprotonated **2c** an intramolecular hydrogen bond can be formed between a phenolic hydroxyl function and a tertiary amine group (see Figure 2a). Evidence for such a bond was found in the infrared spectrum of **2c** in $CDCl_3$, which displayed a relatively sharp signal for a free phenolic hydroxyl function (ν = 3604 cm^{-1}) as well as a broad signal for a hydrogen bonded one (ν = 3327 cm^{-1}).[15] The concentration was taken such (*ca.* 8 mM) that *inter*molecular hydrogen bonding could be excluded. The stretching frequencies of the carbonyl functions of the glycoluril unit ($\nu_{C=O}$ = 1716 and 1692 cm^{-1})[16] remained unaffected, indicating that these are not involved in the hydrogen bonding process. The protons of the benzyl spacers gave rise to only one AB pattern in the ^{1}H NMR spectrum. Moreover, these signals had shifted to higher field as compared to the *ortho*- and *meta*-proton signals of the reference compound $HOC_6H_4CH_2NH_2$. On the basis of these data, we propose that one of the *p*-hydroxybenzyl groups of **2c** is clamped between the side walls of the cleft, as is shown in Figure 2a, and that the in−out movement of this group is a rapid process on the NMR time scale.

The ^{1}H NMR spectrum of the protonated derivative **2c**·2HCl in DMSO-d_6 revealed a complex pattern for the protons of the benzyl spacers. This result suggests that also in this molecule one of the benzyl groups is clamped between the walls. In contrast to **2c** the exchange now is slow on the NMR time scale. This feature may be the result of various hydrogen bonds present in the molecule (see Figure 2b), *viz.* a bond between a quaternized amine and an adjacent carbonyl moiety on one side of the glycoluril unit, a bond between a phenolic hydroxyl function and a protonated amine on the other side of the molecule, in which the former is the H-bond acceptor and the latter the H-bond donor, and a hydrogen bond between the last-mentioned phenolic hydroxyl group and a carbonyl moiety in which the phenol group is the donor. In the IR spectrum of **2c**·2HCl the stretching frequencies of the carbonyl functions of the glycoluril unit had shifted to $\nu_{C=O}$ = 1691 cm^{-1} and an intense broad OH signal was observed in the region from 3000 to 3600 cm^{-1}. Moreover, a weak broad signal at 1900 cm^{-1} was visible, which can be attributed to the $\equiv N^+-H$ vibrations. All these observations are in line with the structure proposed in Figure 2b.

Reaction of **2c** with diphenyl phosphochloridite in CH_2Cl_2 with Et_3N as a base gave the corresponding bis(triaryl phosphite) **2d** (96%). The same result was obtained with **2c**·2HCl when an excess of Et_3N was used. Compound **2d** was fully characterized by elemental analysis and spectroscopic methods.

Rh(I)−Diketonate Complexes. The addition of an equimolar amount of (acac)Rh(CO)$_2$ (Hacac = acetylacetone) to a solution of ligand **2d** in $CHCl_3$ led to the substitution of the carbonyl ligands in the rhodium complex and the formation of metallocage **3a**. The ^{31}P NMR spectrum of **3a** displayed a set of four resonances which had different intensities (Figure 3a and Table 1). Space-filling models suggest that these signals may be attributed to four different conformations of **3a** prescribed by the square-planar coordination of the metal center in combination with the rigidity of the spacers. The interconversions of these conformers, which will be discussed below, require considerable rearrangements in the molecule. These interconversions are slow processes, as was demonstrated by ^{31}P NOESY. Since no cross peaks were observed with a mixing time of 1 s, the lifetime of a single conformation is at least that period.

When more than 1 equiv of (acac)Rh(CO)$_2$ was added to **2d** an additional doublet became visible in the ^{31}P NMR spectrum at δ = 117.8 (J_{Rh-P} = 292 Hz). We assign this signal to the dirhodium complex **4**, which is analogous to the complex (acac)RhCO[P(OPh)$_3$].[17] This suggests that the chelating ability of ligand system **2d** is moderate. No polymeric structures were formed. Apparently, compound **4** is free of strain as only one doublet in the ^{31}P NMR spectrum was observed.

The geometrical isomers of **3a** can be divided into two sets in which the diketonate ligand has either an upward (**U**) or a downward (**D**) orientation with respect to the substrate-binding moiety (see Figure 4). One of the conformers of the **U** set, the **U$_1$** form, is flexible: the rhodium complex is situated above the cavity and can twist easily. The metal center in this conformation is very mobile with regard to the host molecule. In this form the cavity is best accessible for a guest molecule.

(13) (a) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533. (b) Hancock, R. D.; Martell, A. E. *Chem. Rev.* **1989**, *89*, 1875.

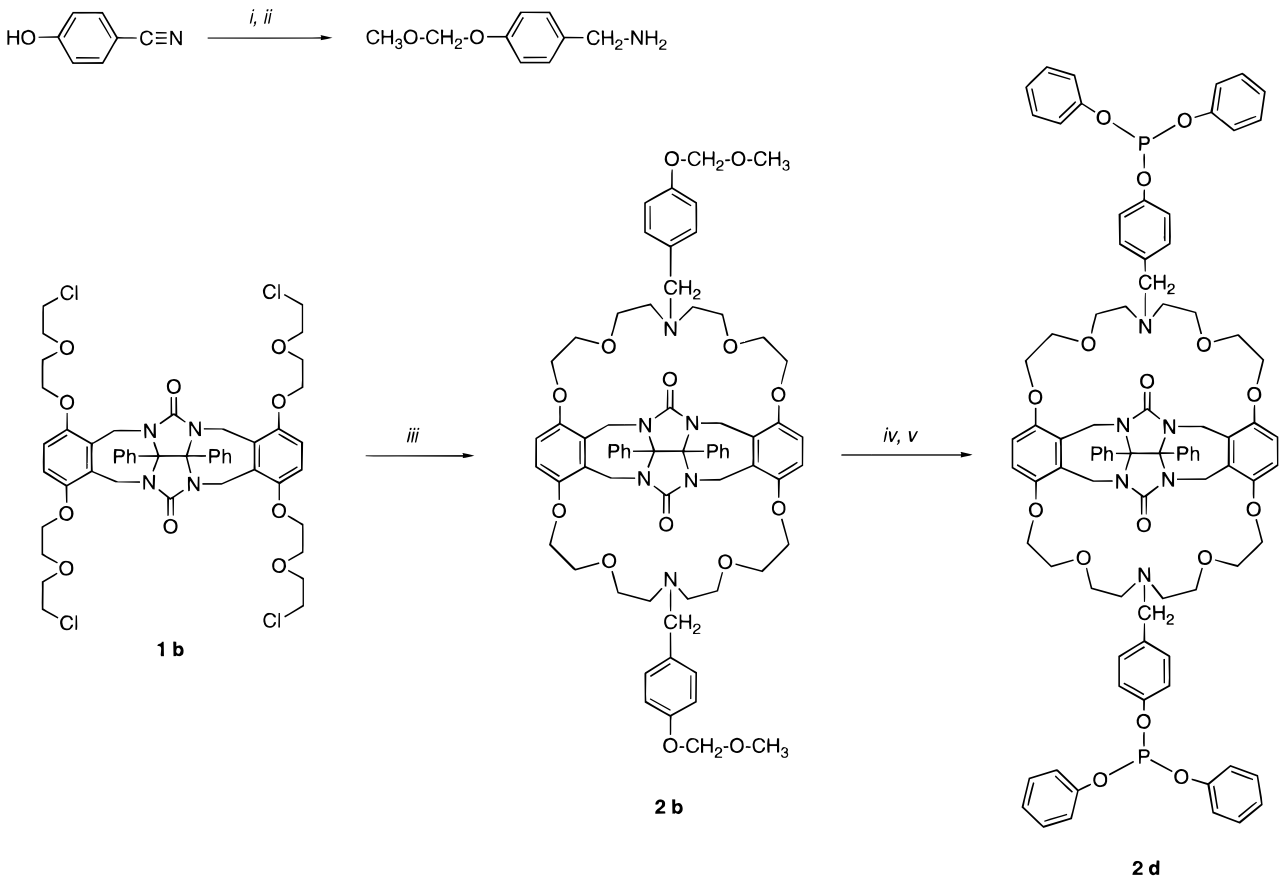
(14) Sijbesma, R. P.; Nolte, R. J. M. *Recl. Trav. Chim. Pays-Bas* **1993**, *112*, 643.

(15) Vinogradov, S. N.; Linnell, R. H. *Hydrogen Bonding*; Van Nostrand Reinhold Co.: New York, 1971; Chapters 3 and 6.

(16) The $\tilde{\nu}$ (C=O) of the free host molecule is split into at least two bands, probably caused by coupling of the C=O vibration with the C−N stretching vibration. See: Sijbesma, R. P. Ph.D. Thesis, University of Nijmegen, 1992, and ref 13.

(17) (a) Trzeciak, A. M.; Ziołkowski, J. J. *Inorg. Chim. Acta* **1982**, *64*, L267. (b) van Eldik, R.; Aygen, S.; Kelm, H.; Trzeciak, A. M.; Ziołkowski, J. J. *Trans. Met. Chem.* **1985**, *10*, 167.

Scheme 1[a]



[a] (i) $ClCH_2OCH_3$, $CH_2Cl_2/H_2O/NaOH/PTC$; (ii) AlH_3, THF; (iii) *p*-$CH_3OCH_2OC_6H_4CH_2NH_2$, Na_2CO_3/NaI, MeCN; (iv) THF/*i*-PrOH/HCl; (v) $ClP(OPh)_2/Et_3N$, CH_2Cl_2.

The other conformer of the **U** set, (**U_2** form), is characterized by the fact that one of the phenyl groups of the triphenyl phosphite ligands is located in the cleft of the host molecule.

The **U** conformers can be converted into **D** conformers by a process in which two phenyl rings of a phosphite ligand pass through the ring formed by the rhodium center, the spacer arms, and the receptor molecule. In fact, the **U_2** form can be regarded as an intermediate on the route of **U_1** to these **D** conformers.

Once in a downward position the diketonate ligand can have two orientations. The most compact structure is obtained when this ligand is located in the cavity (**D_1** conformer), but this arrangement is only possible for diketonate ligands with small substituents. As indicated by CPK models, the sterically less hindered conformation is **D_2**, in which the diketonate ligand is situated next to the cleft and the benzyl spacers are partly covering the cavity.

In order to obtain more information about the conformational behavior of the metallocage we also synthesized complexes **3b**,**c** using (dbm)$Rh(CO)_2$ and (dpm)$Rh(CO)_2$ as starting complexes (Hdbm = dibenzoylmethane, Hdpm = dipivaloylmethane). In contrast to **3a**, compounds **3b**,**c** displayed only three resonances in their ^{31}P NMR spectra (Figure 3b,c and Table 1). The signal attributed to the **D_1** conformer is absent because this geometric arrangement is not possible as a result of the bulky substituent on the diketone ligand.

The different conformations of **3a**−**c** possess varying degrees of symmetry. In the ^1H NMR spectra of these complexes specific signals can be found in which the extent of symmetry is expressed. By correlating the ^1H NMR and ^{31}P NMR signals and taking into account the different intensities we were able to make the assigments listed in Table 1. In addition the following comments can be made.

Several AX patterns, originating from the methylene-bridge protons between the glycoluril unit and the side walls (Figure 5, e) were present in the ^1H NMR spectrum. It was not possible to assign them unequivocally to each of the conformations. In all conformations the proton signals of the aromatic walls (d) gave rise to a complex pattern because of the interference by the aryl groups of the phosphite ligands (Table 1).

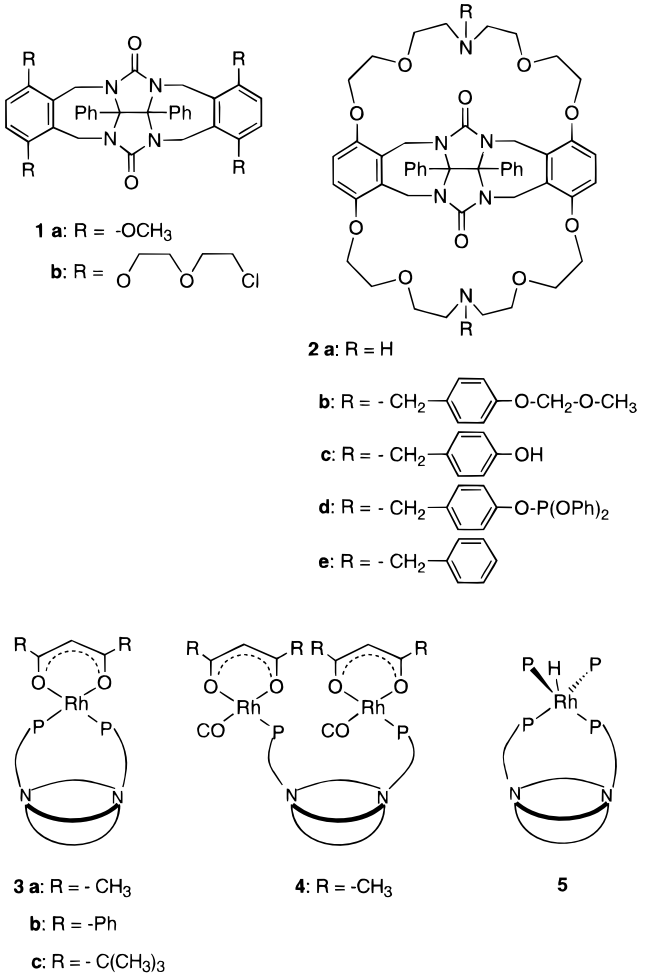
The protons f in the crown ether rings in the **U_1** conformers were visible as a broad signal, reflecting the fluxional movement of the metal complex parts.

The **U_2** conformers were identified by the fact that their ^{31}P NMR resonances disappeared after addition of a substrate molecule (vide infra).

The shoulder on the CH_3 signal at $\delta = 1.49$, belonging to the **U_1** conformer of **3a**, was assigned to the methyl groups of the acetylacetonate ligand of the **D_1** conformer. Despite the fact that these methyl groups are located in the cleft their shift is small as compared to that of the methyl groups in the **U_1** conformation. The reason for this may be that these groups are positioned just outside the shielding zone of the side walls.[11a] Further support for this assignment came from the binding experiments (vide infra).

The **D_2** conformers were identified on the basis of the methylene protons next to the nitrogen atoms in the crown ether ring (Figure 5, protons f). These protons displayed an AA′BB′ pattern which is the result of the asymmetric arrangement of the diketonate ligand.

Chart 1



In the $\mathbf{D_2}$ conformations the rings containing the triphenyl phosphite ligands are rather constrained, which causes the ^{31}P signal to shift to higher fields (see Figure 3).[18] The sharp singlets at $\delta = 6.63$ in the ^1H NMR spectra of the complexes were attributed to the most exposed set of d protons in the $\mathbf{D_2}$ conformations (the wall protons on the right-hand side of the complex in Figure 4d).

To confirm the existence of different conformational isomers and to support the assignment of the individual signals we carried out ^1H NOESY measurements. The 2D spectra of **3a**−**c** revealed both positive and negative cross peaks. The sign of the nuclear Overhauser enhancement is determined by the relaxation pathway.[19] The transitions are stimulated by the fluctuating fields induced by the rotation of the dipoles in solution and are characterized by the correlation time τ_c. For common organic compounds with low molecular weights in non-viscous solvents τ_c is short, *i.e.* the tumbling rate $1/\tau_c$ is fast with respect to the spectrometer frequency (ω), so that $\omega\tau_c < 1.2$. Under these conditions the NOEs are positive. On the other hand, if $\omega\tau_c > 1.2$, the NOEs are negative.[20] For a rigid molecule one single correlation time τ_c applies. When internal motion plays a role it is possible to define effective correlation times $\tau_e < \tau_c$ for

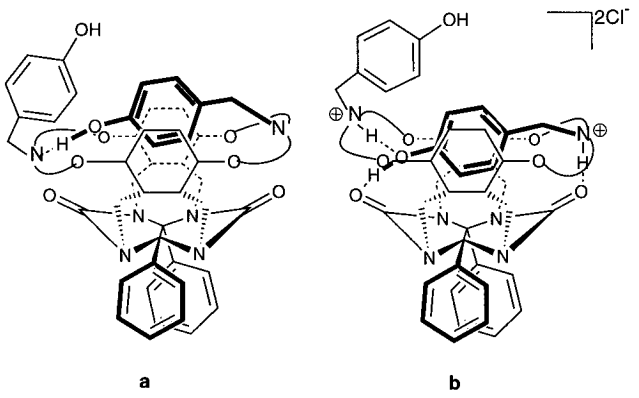


Figure 2. Proposed structures of **2c** (a) and **2c**·2HCl (b).

sections in the molecule.[21] As a result for a molecule with $\omega\tau_c > 1.2$ both positive and negative NOEs may be observed.

In Figure 6 the ^1H NOESY spectrum of compound **3b** is shown. The spectra of **3a**,**c** displayed very similar features. All of the NOEs originating from the host molecule itself, *e.g.* between the geminal protons (e) (Figure 5) of the bridging methylene groups (Figure 6, a) and between the latter protons and the ortho protons (g) (Figure 6, b), were negative, indicating that this part of the molecule is rigid and tumbling slowly. Enhancements coming from the diketonate ligand were either positive or negative, depending on the conformation of the entire molecule. The negative cross peaks were more intense than the positive ones, in accordance with theory.[20] In the $\mathbf{D_2}$ conformation, the diketonate ligand is in a more or less fixed position next to the cavity and its movement is coupled to that of the framework of the molecule. As a result, the interactions between the protons i and h of the diketonate ligand give rise to negative NOEs. On the contrary, in the $\mathbf{U_1}$ conformation the metal complex part is rather mobile and its movement is virtually independent of that of the host molecule, resulting in positive NOEs between protons h and i (Figure 6, c). The benzylic CH_2 groups act as a pivot point in the fluxional movement and therefore their protons (b) displayed only weak negative NOEs with the neighboring protons (a) (Figure 6, d) and with the methylene protons (f).

In a control experiment we confirmed that the sign of the NOE indeed depends on the mobility of the diketonate ligand. The methyl protons of the acetylacetonate ligand in (acac)Rh[$P(OPh)_3$]$_2$ generated a *positive* enhancement of 22% at the methynic proton (i). In **3a** the same protons gave a net *negative* NOE of 22%, which is the sum of contributions from the $\mathbf{U_1}$ (positive enhancement) and the $\mathbf{D_2}$ conformations (negative enhancement).

For the $\mathbf{D_2}$ conformation two different negative NOEs between the aromatic wall protons (d) and the methylene protons (c) were observed, *viz.* one originating from the exposed d protons (*sharp* singlet in the ^1H NMR spectrum) and one coming from the d protons that are covered by the metal complex part (complicated proton signals in the ^1H NMR spectrum) (Figure 6, e). This observation is in line with the asymmetry of the $\mathbf{D_2}$ conformation. The positive NOE between the d and c protons in the spectrum arises from contacts in the $\mathbf{U_1}$ conformation.

The factors that determine the preference for a certain conformation are not fully understood yet. For all

(18) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.
(19) (a) Derome, A. E. *Modern NMR Techniques for Chemistry Research*; Pergamon Press Ltd.: Oxford, U.K., 1987. (b) Sanders, J. K. M.; Hunter, B. K. *Modern NMR Spectroscopy*; Oxford University Press: Oxford, U.K., 1987.
(20) Ernst, R. R.; Bodenhausen, G.; Wokaun, A. *Principles of NMR in One and Two Dimensions*; Clarendon Press: Oxford, U.K., 1987.
(21) Lipari, G.; Szabo, A. *J. Am. Chem. Soc.* **1982**, *104*, 4546.

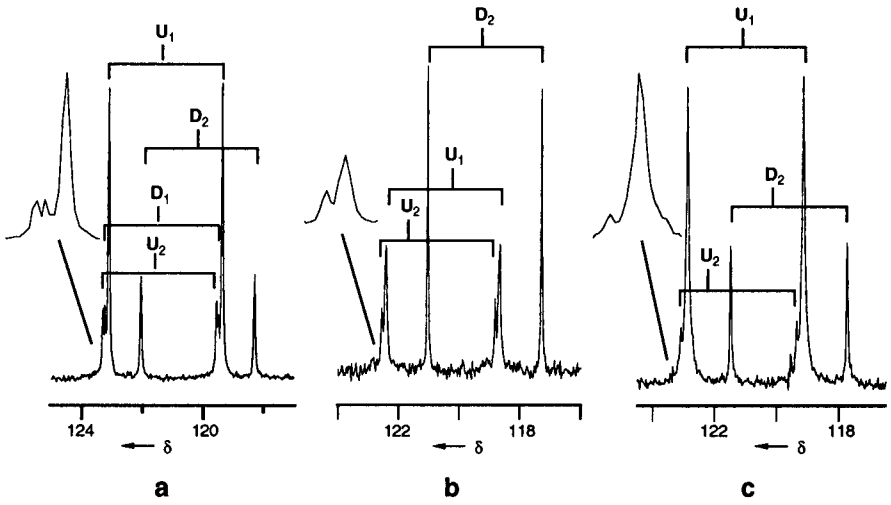


Figure 3. $^{31}P\{^1H\}$ NMR spectra of **3a** (a), **3b** (b), and **3c** (c).

Table 1. NMR Data of Compounds 3a−c

			^1H NMR[b,c]			
compd	conformer	^{31}P NMR[a]	H(d)	H(f)	H(i)	H(h)
3a	U_1	121.2 [304]		2.88 (br)	5.06	1.49
	U_2	121.4 [304]	6.67 6.65 6.63	−	−	−
	D_1	121.3 [304]	6.62 6.56	−	−	−
	D_2	120.2 [304]		2.7−2.85 (m)	5.07	1.51
3b	U_1	120.5 [304]		2.84 (br)	6.55	7.53 (7)[d]
	U_2	120.7 [303]	6.60 6.59 6.53	−	−	−
	D_2	119.1 [305]	6.53	2.6−2.8 (m)	6.49	7.53 (7)
3c	U_1	121.0 [302]		2.88 (br)	5.57	0.86
	U_2	121.2 [303]	6.67 6.63 6.58	−	−	−
	D_2	119.6 [303]		2.68−2.83 (m)	5.57	0.84

[a] δ in ppm [J_{Rh-P} (Hz)] at 80 MHz, referenced to external $OP(OMe)_3$ at 298 K in $CDCl_3$. [b] δ in ppm [J (Hz)] at 400 MHz, referenced to internal TMS at 298 K in $CDCl_3$. [c] Abbreviations used are d = doublet, m = multiplet, br = broad; (−) no assignment could be made; the protons are denoted as shown in Figure 5. [d] Ortho protons of the phenyl rings of the dbm ligand.

compounds **3** the $\mathbf{U_2}$ and the $\mathbf{D_1}$ forms are minor conformations. The more bulky metallohosts **3b**,**c** tend to prefer the $\mathbf{D_2}$ conformation, and at higher temperatures, the $\mathbf{U_1}$ form is slightly preferred by all compounds. An important factor is the amount of water present. This water can be bound in the cavity of the metallohost and can force the latter to adopt its most accessible conformation ($\mathbf{U_1}$).

Rh(I)−Hydride Complexes. Reaction of compounds **3** with H_2 in the presence of a small excess of $P(OPh)_3$ in chloroform led to the formation of the hydride compound **5**. This compound can be isolated by precipitation in hexane but is not stable for long periods of time. In the reference compound $HRh[P(OPh)_3]_4$[22] the Rh center is tetrahedrally surrounded by the phosphites. The hydride is positioned along one of the trigonal axes of the complex. The four phosphites have the same chemical shift and they couple strongly to each other. Hence they give rise to a single resonance in the ^{31}P NMR spectrum (J_{Rh-P} = 229 Hz). This virtual equivalence of the phosphorus atoms is also expressed in the ^1H NMR spectrum by the appearence of a double quintet for the hydride signal (J_{P-H} = 44 Hz, J_{Rh-H} = 3 Hz).[22]

In the case of compound **5** a complex set of signals was visible in the ^{31}P NMR spectrum. The pattern was dependent on the amount of triphenyl phosphite present in solution (Figure 7). In the case of an excess of $P(OPh)_3$ also the signal of uncoordinated phosphites of **2d** became visible besides signals for free $P(OPh)_3$ and **5** (Figure 7b,c). This suggests that in the presence of additional $P(OPh)_3$ the chelated form of **5** (Figure 8, **5a**) is in equilibrium with a form (**5b**) in which one of the ligands of the receptor molecule is replaced by a $P(OPh)_3$ ligand. Other structures can also be imagined, *e.g.* one in which each of the phosphorus atoms of the ligand system is coordinated to a different rhodium center (**5c**) or one in which the rhodium center is chelated by two ligand systems (**5d**). These structures, however, are less likely when equal amounts of ligand **2d** and rhodium are present. They may become important at lower or higher ligand to rhodium ratios. A polymeric form is also conceivable but entropically unfavorable, and not in agreement with the fact that the signals in the ^1H NMR spectrum are relatively sharp. We assign the complex signal in the ^{31}P NMR spectrum after isolation of the metallohost to structure **5a**. The complexity of the signal may arise from a distortion of the tetrahedral arrangement of the phosphites around the rhodium center, due to the bulky ligand system. As compared to HRh-

(22) (a) Levison, J. J.; Robinson, S. D. *J. Chem. Soc., Chem. Commun.* **1968**, 1045. (b) Coolen, H. K. A. C.; Nolte, R. J. M.; van Leeuwen, P. W. N. M. *J. Organomet. Chem.* **1995**, *496*, 159.

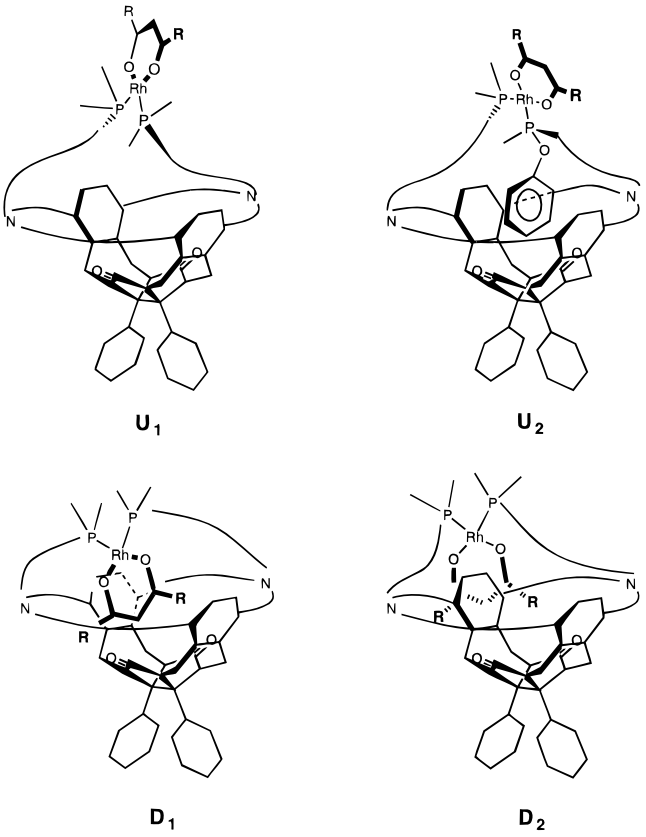


Figure 4. Schematic representations of the different conformations of metallohost **3**.

$[P(OPh)_3]_4$ this could lead to a considerable change in the magnitude of the couplings between the different phosphorus atoms and between the phosphorus atoms and the rhodium center.[23] In **5b**, there is no need for a distortion and the phosphorus atoms will give rise to a single doublet, comparable to $HRh[P(OPh)_3]_4$. In Figure 7b−d this doublet is superimposed on the signal of **5a**.

The signal in Figure 7a cannot be simulated to fit an A_2B_2 pattern. Such a pattern would be expected if one of the C_{2v} symmetry planes of the basket of **5** laterally bisects one of the T_d symmetry planes of the metal complex. Apparantly, the metal complex part is slightly twisted with respect to the receptor molecule thereby cancelling the symmetry in the system. As a result all of the phosphorus atoms have become chemically and magnetically unequivalent. When more than 2 equiv of $P(OPh)_3$ is added the fine structure of the ^{31}P NMR signal is lost probably as a result of broadening due to ligand exchange. Additionally, the signal sharpens because compound **5b** becomes dominant (Figure 7c,d).

The signal of the hydride ligand in the high-field ^1H NMR spectrum of **5** was broadened, probably for two reasons: (*i*) the nonequivalence of the phosphorus atoms and (*ii*) the fact that the two pairs of faces of the rhodium tetrahedron are unequal (the hydride ligand can point toward the cavity or away from it). In Figure 9 this hydride signal is shown for a solution of **5** containing approximately an additional 4 equiv of $P(OPh)_3$. The sharp signals originating from structure **5b** are superimposed on the broad signals of structure **5a**.

Compound **5** could also be obtained by an exchange reaction in which two of the $P(OPh)_3$ ligands of $HRh[P(OPh)_3]_4$ are displaced by the phosphite ligands of **2d**. After addition of an equimolar amount of $HRh[P(OPh)_3]_4$ to a solution of **2d** in chloroform, signals for **5**, for the uncoordinated phosphites of **2d**, as well as for free $P(OPh)_3$ were clearly resolved in the ^{31}P NMR spectrum. By integration of these signals the equilibrium constant for the process **5a** + $P(OPh)_3 \rightleftarrows$ **5b** could be determined. This constant amounted to $K_{ab} = 0.034\ M^{-1}$. This value implies that in the presence of an extra 2 equiv of $P(OPh)_3$ still 94% of the rhodium is in the chelated form **5a**. If only an additional 1 equiv of phosphite is present this percentage is 97%. Apparently, in spite of the fact that **2d** has a large ring, the ligand exerts a substantial chelate effect.

Binding Properties. Recent studies in our group have shown that basket-shaped compounds of type **2** can complex dihydroxybenzene guests.[24] Binding occurs by means of hydrogen bonds between the hydroxyl substituents of the guest and the carbonyl functions of the glycoluril unit and depending on the type of guest also by hydrogen bonding with the crown ether fragments. In addition to this the host−guest complex is stabilized by π-stacking interactions between the benzene ring of the guest and the aromatic side walls of the host. The binding properties of the metallohosts were evaluated by ^1H and ^{31}P NMR spectroscopy monitoring the shifts and intensities of appropriate signals of the host−guest complex.

The addition of a substrate was found to affect the conformational behavior of complexes **3a**−**c** considerably (Figure 10). In the presence of resorcinol, the signals for the $\mathbf{U_2}$ conformation in the ^{31}P NMR spectra disappeared completely. Apparently, the substrate dispels the aromatic ring of the triphenyl phosphite ligand out of the cleft. Furthermore, the binding of a substrate induced a change of the $\mathbf{D_2}$ into the $\mathbf{U_1}$ conformation, probably because the latter has a less strained cavity. After approximately 2 equiv of substrate hardly any $\mathbf{D_2}$ conformer was left. At that point the ^{31}P signals of the $\mathbf{U_1}$ conformer had slightly shifted to lower field (∼0.1 ppm), whereas the signals of the $\mathbf{D_2}$ conformer had strongly shifted to higher field (∼0.4 ppm). For **3a** addition of resorcinol did not result in the instantaneous disappearance of the ^{31}P signal of the $\mathbf{D_1}$ conformation. In the presence of approximately 0.5 equiv of resorcinol still about 7% of the ^{31}P NMR signal is due to the $\mathbf{D_1}$ conformer (Figure 10a). Only after 5 equiv of substrate had been added did this signal weaken, indicating that the compact $\mathbf{D_1}$ structure with the acetylacetone ligand bent into the cavity is rather stable.

NMR titrations were used to determine the association constant K_a for resorcinol in **3a**−**c**. In order to avoid complications due to **D**−**U** transitions the first points of the titration curve ([host]/[guest] < 2) were not used to calculate the K_a. The values found amounted to K_a = 3100 M^{-1} for **3a** and K_a = 2850 M^{-1} for **3b**, in good agreement with the values measured for the reference compounds **1a** and **2e** (see Table 2).

It was not possible to manipulate solutions of the hydride complex **5** to such an extent that association constants for this complex could be determined quantitatively. However, the observed shifts of mixtures of resorcinol and **5** indicated that the K_a value is in the same

(23) Pregosin, P. S.; Kunz, R. W. *^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes. (NMR, Basic Principles and Progress, part 16)*, 2nd ed.; Diehl, P., Fluck, E., Kosfeld, R., Eds.; Springer-Verlag: Berlin, 1979.

(24) (a) Sijbesma, R. P.; Kentgens, A. P. M.; Nolte, R. J. M. *J. Org. Chem.* **1991**, *56*, 3199. (b) Sijbesma, R. P.; Nolte, R. J. M. *J. Org. Chem.* **1991**, *56*, 3122.

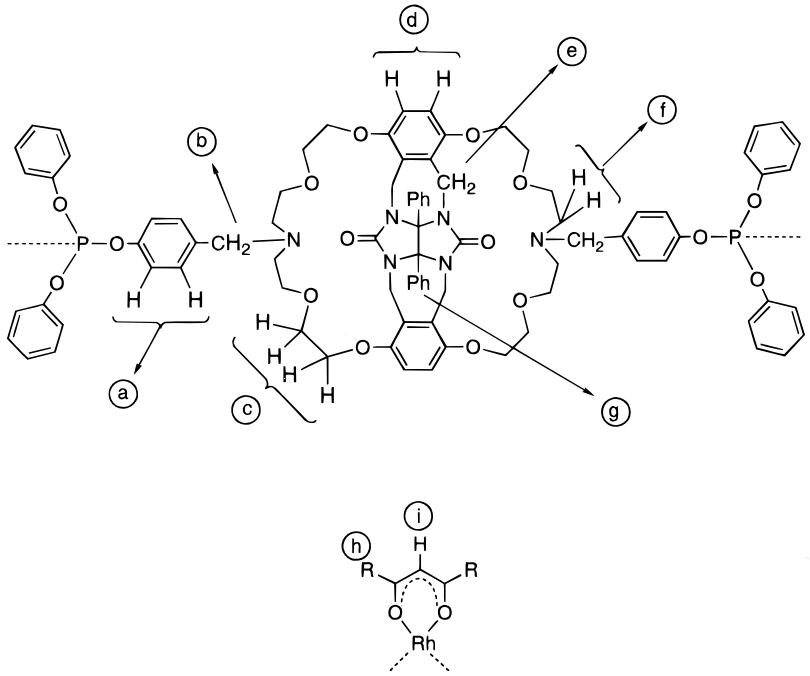


Figure 5. Numbering of H atoms used for the assignment of the ^{1}H NMR signals.

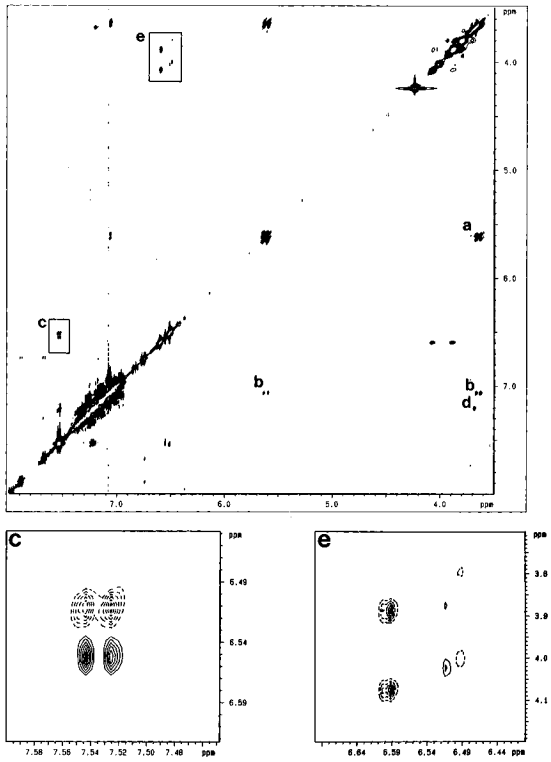


Figure 6. ^{1}H-NOESY of compound **3b** in $CDCl_3$ (τ_m = 0.8 s, T = 298 K). The enlargements of regions **c** and **e** are given separately. The dashed lines indicate that the cross peaks are negative. The splitting of the signals in region **c** is due to coupling with an ortho proton.

range as for **3** (~3000 M^{-1}), assuming that the maximum shift ∂_{max} of the host−guest complex for **5** is appromately the same as that for **3**. After addition of resorcinol to a solution of **5** in chloroform the signals in the ^{31}P NMR spectrum sharpened and the second-order effects disappeared. This suggests that the binding of the substrate forces the system to adopt a more symmetrical geometry. Possibly, the metal complex part is lifted a little with respect to the receptor molecule, which restores the tetrahedral arrangement of the phosphites around the metal center.

Experimental Section

General Procedures. Unless indicated otherwise, commercial products were used as received. Hexane and toluene were distilled under a nitrogen atmosphere from sodium ketyl. Dichloromethane (CH_2Cl_2) and tetrahydrofuran (THF) were distilled from lithium aluminium hydride ($LiAlH_4$). Chloroform and chloroform-d_1 were distilled from phosphorus pentoxide (P_2O_5). All solvents were stored on molecular sieves under an inert atmosphere.

Cyano-4-(methoxymethoxy)benzene. This compound was prepared according to a literature procedure:[25] 16 g (0.2 mmol) of chloromethyl methyl ether was added dropwise to a vigorously stirred two-phase system consisting of 5.96 g (50 mmol) of 4-cyanophenol, 3 g (7.5 mmol) of Aliquat in 250 mL of CH_2Cl_2, and 3 g (75 mmol) of sodium hydroxide in 100 mL of water. After TLC (eluent: acetone−hexane = 1:4 v/v) had indicated the disappearance of the 4-cyanophenol, the layers were separated and the water layer was extracted twice with CH_2Cl_2. The combined organic layers were dried ($MgSO_4$), and the solvent was removed under reduced pressure. The product was purified by column chromatography (silica, eluent: acetone−hexane = 1:4, v/v) to yield 4.23 g (52%) of a yellowish oil that solidified on cooling: ^{1}H NMR (90 MHz, $CDCl_3$) δ 7.59 (d, J = 9 Hz), 7.09 (d, J = 9 Hz), 5.22 (s), 3.48 (s).

***p*-(Methoxymethoxy)benzylamine.** This compound was prepared according to a literature procedure[26] using 4.2 g (25.7 mmol) of cyano-4-(methoxymethoxy)benzene, 1.47 g (38.6 mmol) of $LiAlH_4$, and 1.89 g (19.3 mmol) of sulfuric acid in 80 mL of THF; yield 3.2 g (75%) of product as a yellow oil; ^{1}H NMR (90 MHz, $CDCl_3$) δ 7.23 (d, J = 9 Hz), 7.00 (d, J = 9 Hz), 5.16 (s), 3.80 (s), 3.47 (s), 1.66 (s).

5,7,12,13b,13c,14-Hexahydro-1,4,8,11-tetrakis[2-(2-chloroethoxy)ethoxy]-13b,13c-diphenyl-6*H*,13*H*-5a,6a,12a,-13a-tetraazabenz[5,6]azuleno[2,1,8-*ija*]benz[*f*]azulene-6,13-dione (1b). This compound was synthesized as described in ref 14.

2a,8,9,12,13,14,15,17,18,25,26,29,30,31,32,34,35,38b-Octadecahydro-2a,38b-diphenyl-13,30-bis[4-(methoxymethoxy)phenylmethyl]-1*H*,4*H*-6,37:20,23-dietheno-2,22:

(25) van Heerden, F. R.; van Zyl, J. J.; Rall, G. J. H.; Brandt, E. V.; Roux, D. G. *Tetrahedron Lett.* **1978**, 661.

(26) Yoon, N. M.; Brown, H. C. *J. Am. Chem. Soc.* **1968**, *90*, 2927.

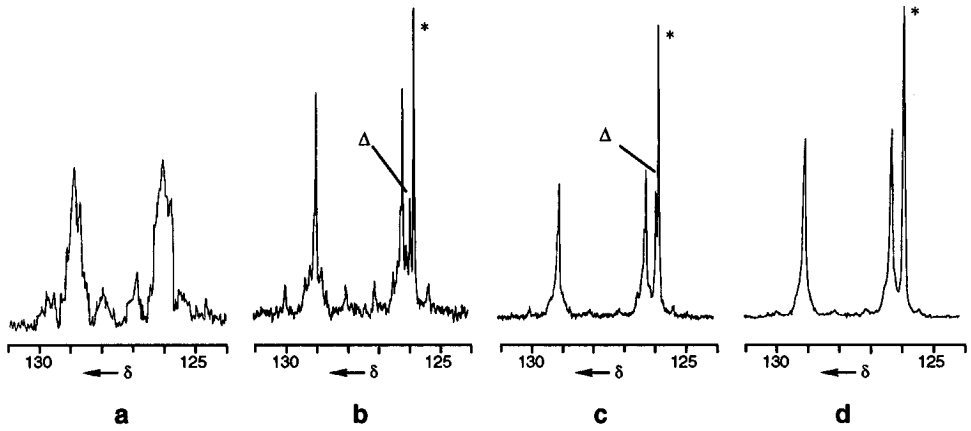


Figure 7. $^{31}P\{^1H\}$ NMR spectra of compound **5** with different amounts of additional $P(OPh)_3$ present: after isolation (no extra triphenyl phosphite) (a) and with 2 equiv (b), with *ca.* 4 equiv (c), and with *ca.* 6 equiv (d) of extra $P(OPh)_3$. The signal of free $P(OPh)_3$ is marked with an asterisk and that of an uncoordinated phosphite ligand of **2d** with a triangle.

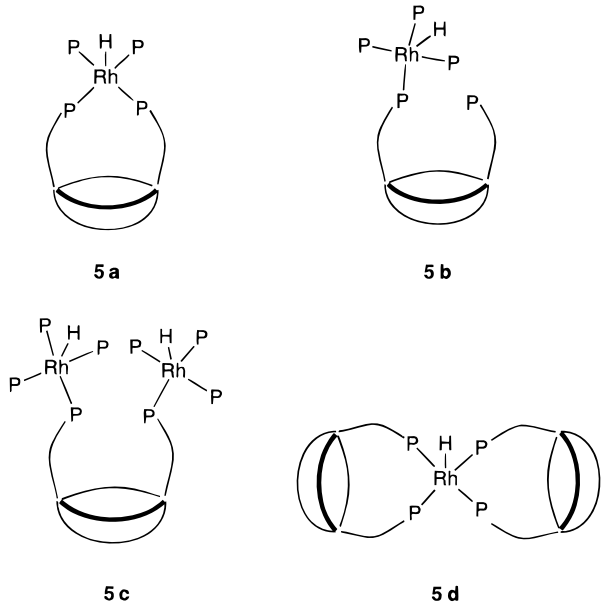


Figure 8. Schematic representation of the different rhodium hydride complexes derived from **2d.**

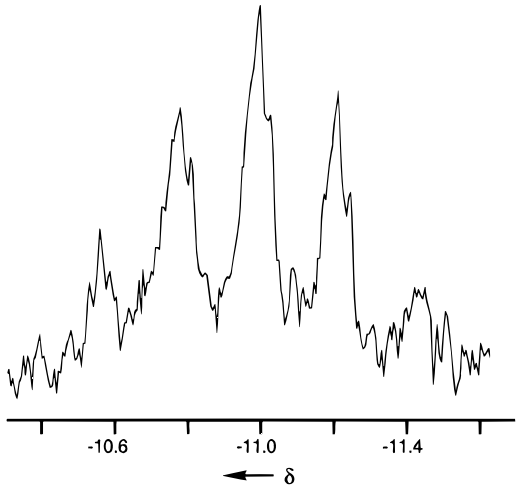


Figure 9. Hydride region of the ^1H NMR spectrum of **5** in the presence of approximately an additional 4 equiv of $P(OPh)_3$. The sharp signals of structure **5b** are superimposed on the broad signals of structure **5a**.

3,21-dimethano-5*H*,11*H*,28*H*,38*H*-7,10,16,19,24,27,33,36-octaoxa-2,3,4a,13,30,38a-hexaazacyclopenta[*cd*]cyclotetratriacont[*g*]azulene-1,4-dione (2b). This compound was prepared according to a procedure developed in our laboratory[14] using 5 g (5.1 mmol) of **1b**, 2.52 g (15.2 mmol) of *p*-(methoxymethoxy)benzylamine, 16.25 g of Na_2CO_3 (0.15 mol), and 50 g of NaI in 1.5 L of acetonitrile. The product was purified by column chromatography using gradient elution (silica, eluent: $CHCl_3$ with 1% Et_3N and 0.5%−1% methanol): yield 4.45 g (75%) of white **2b**; ^1H NMR (90 MHz, $CDCl_3$) δ 7.31(d, J = 9 Hz), 7.11 (s), 6.98 (d, J = 9 Hz), 6.74 (s), 5.69 (d, J = 16 Hz), 5.18 (s) 4.26−3.57 (m), 2.89 (tr, J = 6 Hz); FAB-MS m/z 1178 ($[M + H]^+$). Anal. Calcd for $C_{66}H_{76}N_6O_{14}\cdot H_2O$: C, 66.32; H, 6.58; N, 7.03. Found: C, 66.56; H, 6.26; N, 7.04%.

2a,8,9,12,13,14,15,17,18,25,26,29,30,31,32,34,35,38b-Octadecahydro-2a,38b-diphenyl-13,30-bis[(4-hydroxyphenyl)methyl]-1*H*,4*H*-6,37:20,23-dietheno-2,22:3,21-dimethano-5*H*,11*H*,28*H*,38*H*-7,10,16,19,24,27,33,36-octaoxa-2,3,4a,13,30,38a-hexaazacyclopenta[*cd*]cyclotetratriacont[*g*]azulene-1,4-dione Dihydrochloride [2c·2HCl]. To a solution of 2.5 g (2.1 mmol) of compound **2b** in a mixture of 50 mL of THF and 50 mL of isopropyl alcohol was added dropwise 10 mL of concentrated aqueous HCl (30%). After being stirred for 3 h, the solution was evaporated to dryness, and the resulting solid material was dried under high vacuum, to give 2.45 g (100%) of white **2c**·2HCl: ^1H NMR (100 MHz, DMSO-d_6) δ 10.4 (br), 7.56−7.43 (m), 7.15 (s), 6.97−6.60 (m), 6.62 (s), 5.51 (d, J = 16 Hz), 5.45 (d, J = 16 Hz), 4.7−3.2 (br); IR (CsI) $\tilde{\nu}$ (cm^{-1}) = 3448 (OH, br), 1691 (NC(O)N), 1131 (COC); FAB-MS m/z 1089 ($[\mathbf{2c} + H]^+$), 545 ($^1/_2[\mathbf{2c} + 2H]^+$). Anal. Calcd for $C_{62}H_{68}N_6O_{12}\cdot 3HCl\cdot H_2O$: C, 61.21; H, 6.05; N, 6.91. Found: C, 61.99; H, 6.04; N, 6.80%.

The compound can be deprotonated to **2c** with a $NaHCO_3$/NaOH buffer of pH = 9.75 (2.1 g of $NaHCO_3$ and 0.4 g of NaOH in 600 mL of water): ^1H NMR (400 MHz, $CDCl_3$) δ 7.16−7.10 (m), 6.93 (d, J = 7.5 Hz), 6.32 (s), 6.23 (d, J = 7.5 Hz), 5.67 (d, J = 16 Hz), 4.02−3.60 (m), 2.79 (s br); IR ($CDCl_3$) $\tilde{\nu}$ (cm^{-1}) = 3604 (ArOH free), 3327 (ArOH bridged), 1716, 1692 (NC(O)N); FAB-MS m/z 1089 ($[M + H]^+$). Anal. Calcd for $C_{62}H_{68}N_6O_{12}\cdot NaCl$: C, 64.88; H, 5.97; N, 7.32. Found: C, 64.73; H, 6.05; N, 7.04%.

2a,8,9,12,13,14,15,17,18,25,26,29,30,31,32,34,35,38b-Octadecahydro-2a,38b-diphenyl-13,30-bis[[4-(diphenylphosphito)phenyl]methyl]-1*H*,4*H*-6,37:20,23-dietheno-2,22:3,-21-dimethano-5*H*,11*H*,28*H*,38*H*-7,10,16,19,24,27,33,36-octaoxa-2,3,4a,13,30,38a-hexaazacyclopenta[*cd*]cyclotetratriacont[*g*]azulene-1,4-dione (2d). Under an inert atmosphere 2.7 g (10.8 mmol) of diphenyl phosphochloridite was slowly added to a solution containing 2.5 g (2.15 mmol) of **2c**·2HCl, 30 mL of CH_2Cl_2, and 2.1 mL (15.1 mmol) of Et_3N. The mixture was refluxed for 2.5 h with stirring. The reaction volume was reduced to 5 mL and added dropwise to 150 mL of dry hexane. The resulting precipitate was filtered off, washed twice with hexane, and dried under vacuum. The solid was dissolved in 100 mL of CH_2Cl_2 and washed 4× with a $NaHCO_3$/NaOH buffer (pH = 9.5). The organic layer was dried ($MgSO_4$) and evaporated to dryness, and the resulting product

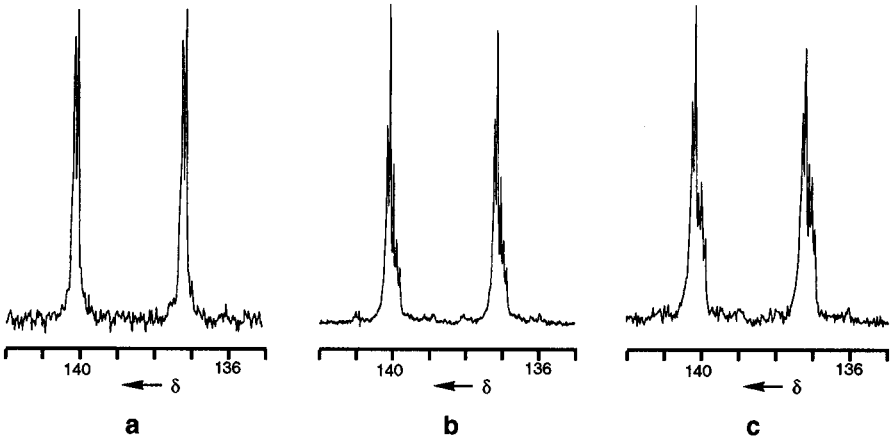


Figure 10. $^{31}P\{^1H\}$ NMR spectra of **3a** (a), **3b** (b), and **3c** (c) in the presence of approximately 0.5 equiv of resorcinol.

Table 2. Association Constants of Complexes between Different Hosts and Resorcinol in $CDCl_3$

host	K_a/M^{-1} [a]	ref
1a	2600	25a
2e	2900	25b
3a	2850	this work
3b	3100	this work

[a] Estimated error: 10−15%.

was dried under high vaccuum: yield 3.09 g (94%) of foamy white **2d**; ^{31}P NMR (80 MHz, $CDCl_3$) δ 125.9; ^1H NMR (400 MHz, $CDCl_3$) δ 7.36−7.04 (m), 6.68 (s), 5.66 (d, J = 16 Hz), 4.15−3.67 (m), 2.89 (tr, J = 5.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 151.7, 129.6, 120.7, 124.2, 150.4, 134.0, 129.3, 119.1, 150.7, 128.6, 113.8, 130.2, 128.6−128.3, 85.1, 69.9, 69.6, 69.4, 59.1, 53.7, 36.9; IR (CsI) $\tilde{\nu}$ (cm^{-1}) = 1712 (NC(O)N), 1197 (POPh), 504 ($P(OR)_3$); FAB-MS m/z 1522 ($[M + H]^+$). Anal. Calcd for $C_{86}H_{86}N_6O_{16}P_2$: C, 67.89; H, 5.70; N, 5.52. Found: C, 67.47; H, 5.84; N, 5.29%.

Rhodium Dicarbonyl Dibenzoylmethanoate [(dbm)-Rh(CO)$_2$]. This complex was prepared according to a modified literature procedure:[27] 200 mg (0.76 mmol) of $RhCl_3 \cdot 3H_2O$ and 0.5 g (2.23 mmol) of dibenzoylmethane in 4 mL of dimethylformamide (DMF) was refluxed for 1 h. During that time the solution became orange. After cooling, 10 mL of a 0.5 N aqueous NaOH solution was added and the dark precipitate was filtered off, subsequently washed with water, cold ethanol, and cold ether, and dried. The product was extracted from the solid material with hot hexane. After evaporation of the solvent 142 mg (49%) of (dbm)$Rh(CO)_2$ was obtained as orange flakes: ^1H NMR (90 MHz, $CDCl_3$) δ 8.83−7.77 (m), 7.66−7.31 (m), 6.94 (s); IR (CsI) $\tilde{\nu}$ (cm^{-1}) = 2963 (ArH), 2079, 2002 (RhCO), 1541 (CO diketonate), 519 (RhO). Anal. Calcd for $C_{17}H_{11}O_4Rh$: C, 53.43; H, 2.90. Found: C, 54.36; H, 2.98%.

Rhodium Dicarbonyl Dipivaloylmethanoate [(dpm)-Rh(CO)$_2$]. This complex was prepared as described for (dbm)-$Rh(CO)_2$ using 200 mg (0.76 mmol) of $RhCl_3 \cdot 3H_2O$ and 0.42 g (2.28 mmol) of dipivaloylmethane in 4 mL of DMF: yield 196 mg (75%) of (dpm)$Rh(CO)_2$ as flakes with characteristic red-green dichroism; ^1H NMR (90 MHz, $CDCl_3$) δ 5.44 (s), 0.64 (s); IR (CsI) $\tilde{\nu}$ (cm^{-1}) = 2067, 2011 (RhCO), 1548 (CO diketonate), 1362 ($C(CH_3)_3$), 474 (RhO). Anal. Calcd for $C_{13}H_{19}O_4Rh$: C, 45.63; H, 5.6. Found: C, 45.71; H, 5.56%.

Compound 3a. To a solution of 200 mg (0.14 mmol) of ligand **2d** in 20 mL of $CHCl_3$ was added 35.4 mg (0.14 mmol) of (acac)$Rh(CO)_2$. Argon was led through the solution for 15 min to remove the released carbon monoxide. The product was precipitated by first reducing the solvent volume to 2 mL and subsequently adding the resulting solution dropwise to 25 mL of hexane. After filtration and drying under vacuum 201 mg (85%) of **3a** as a yellow solid was obtained: ^{31}P NMR (80 MHz, $CDCl_3$) δ 121.4, 121.3, 121.2, 120.2 (d, J_{Rh-P} = 304 Hz) (see text); ^1H NMR (400 MHz, $CDCl_3$) δ 7.33−7.01 (m), 6.67−6.56 (m), 5.67−5.61 (several d, J = 16 Hz), 5.073 and 5.067 (2 s), 4.12−3.65 (m), 2.88 and 2.82−2.73 (br and m), 1.51 and 1.50 (2 s); IR (CsI) $\tilde{\nu}$ (cm^{-1}) = 1715 (NC(O)N), 1580 (CC, diketone), 1197 (POPh); FAB-MS m/z 1723 (M^+). Anal. Calcd for $C_{91}H_{93}N_6O_{18}P_2Rh$: C, 63.41; H, 5.44; N, 4.88. Found: C, 63.48; H, 5.38; N, 4.87%.

Compound 3b. This compound was prepared in the same way as **3a**, using 195 mg (0.13 mmol) of ligand **2d** and 49 mg (0.13 mmol) of (dbm)$Rh(CO)_2$: yield 200 mg (85%) of **3b** as a yellow solid; ^{31}P NMR (80 MHz, $CDCl_3$) δ 120.7, 120.5, 119.1 (d, J_{Rh-P} = 304 Hz) (see text); ^1H NMR (400 MHz, $CDCl_3$) δ 7.89−6.92 (m), 6.78−6.51 (m), 6.55 and 6.49 (2 s), 5.63 and 5.62 (2 d, J = 16 Hz), 4.07−3.64 (m br), 2.84 and 2.79−2.63 (br and m); IR (CsI) $\tilde{\nu}$ (cm^{-1}) = 1712 (NC(O)N), 1591 (C−C, diketone), 1194 (POPh), 592 (diketone). Anal. Calcd for $C_{101}H_{97}N_6O_{18}P_2Rh$: C, 65.65; H, 5.29; N, 4.55. Found: C, 65.80; H, 5.29; N, 4.40%.

Compound 3c. This compoud was prepared in the same way as **3a** using 180 mg (0.12 mmol) of ligand **2d** and 40 mg (0.12 mmol) of (dpm)$Rh(CO)_2$: yield 200 mg (85%) of **3b** as a yellow solid; ^{31}P NMR (80 MHz, $CDCl_3$) δ 121.2, 121.0, 119.6 (d, J_{Rh-P} = 304 Hz) (see text); ^1H NMR (400 MHz, $CDCl_3$) δ 7.36−6.98 (m), 6.67−6.58 (m), 5.64 (d br, J = 16 Hz), 4.12−3.65 (m), 2.88 and 2.82−2.68 (br and m), 0.86 and 0.84 (2 s); IR (CsI) $\tilde{\nu}$ (cm^{-1}) = 1716 (NC(O)N), 1594 (C−C, diketone), 1359 ($C(CH_3)_3$), 1199 (POPh), 596 (diketone). Anal. Calcd for $C_{97}H_{105}N_6O_{18}P_2Rh$: C, 64.45; H, 5.85; N, 4.65. Found: C, 64.43; H, 5.85; N, 4.67%.

Complex 5. This compound was prepared by following the same procedure as described for compound **3a**. An extra amount of 90 mg (0.29 mmol) of $P(OPh)_3$ was added, and the reaction mixture was stirred for 12 h under 10 atm of hydrogen pressure. The complex was precipitated by first reducing the solvent volume to 2 mL and subsequently adding the resulting solution dropwise to 25 mL of hexane. Complex **5** could also be prepared by the addition of 41 mg (30 mmol) of $HRh[P(OPh)_3]_4$ to a solution of 46 mg (30 mmol) of ligand **2d** in $CHCl_3$: $^{31}P\{^1H\}$ NMR (80 MHz, $CDCl_3$) δ 127.6 (d br, J_{Rh-P} = 229 Hz) (see Figure 7); ^1H NMR (200 MHz, $CDCl_3$) δ 7.6−6.4 (m), 5.63 (d br, J = 16 Hz), 4.3−3.35 (m), 3.15−2.65 (br), −11.0 (qu br) (see Figure 9); due to its limited stability no satisfying elemental analysis could be obtained for this product.

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