Hexahomotrioxacalix[3]arene: a scaffold for a C_3-symmetric phosphine ligand that traps a hydrido-rhodium fragment inside a molecular funnel

Cedric B. Dieleman,[a] Dominique Matt,*[a] Ion Neda,[b] Reinhard Schmutzler,[b] Anthony Harriman[c] and Reza Yaftian[d]

[a] *Groupe de Chimie Inorganique Moléculaire, UMR 7513 CNRS, 1 rue Blaise Pascal, F-67008 Strasbourg Cedex, France. E-mail: dmatt@chimie.u-strasbg.fr*
[b] *Institut für Anorganische Chemie und Analytische Chemie der Universität, Postfach 3329, D-38023 Braunschweig, Germany*
[c] *Ecole Européenne de Chimie, Polymères et Matériaux, 1 rue Blaise Pascal, F-67008 Strasbourg Cedex, France*
[d] *Department of Chemistry, University of Zandjan, PO box 313, 45195 Zandjan, Iran*

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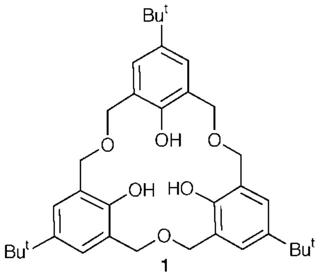
Stereoselectivity around an H–Rh–CO fragment has been realized by reaction of the hexahomotrioxacalix[3]arene-derived triphosphine 4 with [Rh(acac)(CO)$_2$]; the resultant trigonal bipyramidal complex has the Rh–H bond directed inside the cavity.

Phosphorus-bearing calixarenes have received considerable attention both for their ionophoric receptor properties and their facility for localizing reactive transition metal centres adjacent to the cavity.[1] To date, most studies have been concerned with functionalized calix[4]arenes,[2] while the corresponding hexahomotrioxacalix[3]arenes **1** remain relatively unexplored, although such receptors have been equipped with P^{III}- or P^{V}-based binding sites.[3,4] The larger macrocyclic unit provided by **1** looks to be particularly appropriate for use as a platform on which to build C_3-symmetrical ligands able to operate as conical receptors.[5–8] We now describe the synthesis and properties of the first triphosphine ligands, and their corresponding oxides, formed by anchoring CH$_2$P(O)Ph$_2$ groups to the phenolic oxygen atoms of a calix[3] matrix.



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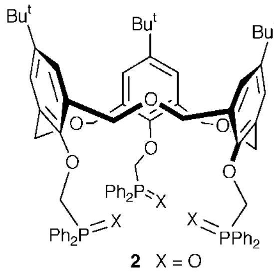
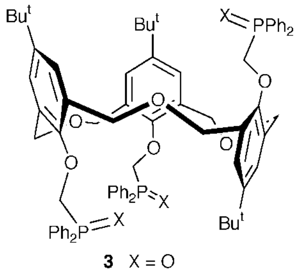


2 X = O
4 X = lone pair



3 X = O
5 X = lone pair

Complete phosphorylation was achieved by reacting **1** with NaH and Ph$_2$P(O)CH$_2$OTs in toluene at 90 °C for three days. The reaction resulted in formation of a 4 : 1 mixture of the (non-interconverting) phosphine oxides **2** and **3**.† Separation by column chromatography afforded pure **2** in 72% yield, but the isolated samples of **3** always contained small amounts of **2**. Consistent with a C_3-symmetrical structure, the ^{31}P NMR spectrum of **2** shows a single peak at δ_P 24.9 while the corresponding ^{1}H NMR spectrum displays a unique AB system for the ArCH$_2$ methylene groups. Compound **3** adopts a partial cone conformation as deduced from the presence of two singlets of intensity 2 : 1 in the ^{31}P NMR spectrum, together with three AB patterns for the ArCH_2 groups in the ^{1}H NMR spectrum. The phosphine oxides **2** and **3** could be reduced with PhSiH$_3$ in refluxing toluene, affording the triphosphines **4** and **5**,† respectively, in quantitative yield. The partial cone structure of **5** (Fig. 1) was confirmed by an X-ray diffraction study.‡ It should be emphasised that compounds **2**–**5** are highly soluble in alkanes.

The triphosphorylated calixarene **2** was found to be an active phase-transfer agent for rare-earth picrates (from water to CH$_2$Cl$_2$).§ Extraction experiments carried out with seven rare-earth cations (Y, La, Pr, Nd, Sm, Eu and Gd) showed the extraction percentages to be significantly higher than those obtained with conventional phosphine oxides, *e.g.* trioctylphosphine oxide, or the phosphato-calix[4]arenes reported recently by Harrowfield *et al.*[9] Interestingly, the highest selectivity was found for those elements with an ionic radius close to that of praseodymium; similar peak selectivity was observed recently with a *cone*-calix[4]arene substituted by four CH$_2$P(O)Ph$_2$ phosphine oxide arms tethered at the lower rim.[10] Our findings confirm previous observations showing that phosphorus-based ligands built on calixarenes may display different extraction properties than do their acyclic counterparts.[11]

Ligand **4** looks to be an ideal scaffold for the formation of C_3-symmetrical complexes. Thus, treatment of **4** with [Mo(CO)$_3$-(cycloheptatriene)] in refluxing THF afforded the colourless complex **6**† in high yield (Scheme 1). The carbonyl region of the IR spectrum displays two strong absorption bands showing the presence of an Mo(CO)$_3$ unit with local C_{3v} symmetry.[12] Tridentate *fac*-coordination of the tripod was inferred from the appearance of a singlet at δ_P 25.7 in the ^{31}P NMR spectrum. In **6**, the tripodal arms retain the metal centre beneath the cavity. Likewise, complex **7**,† formed in quantitative yield on reaction of **4** with [Au(THF)(THT)]PF$_6$ (THT = tetrahydrothiophene),

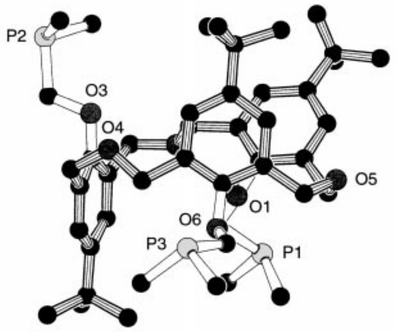
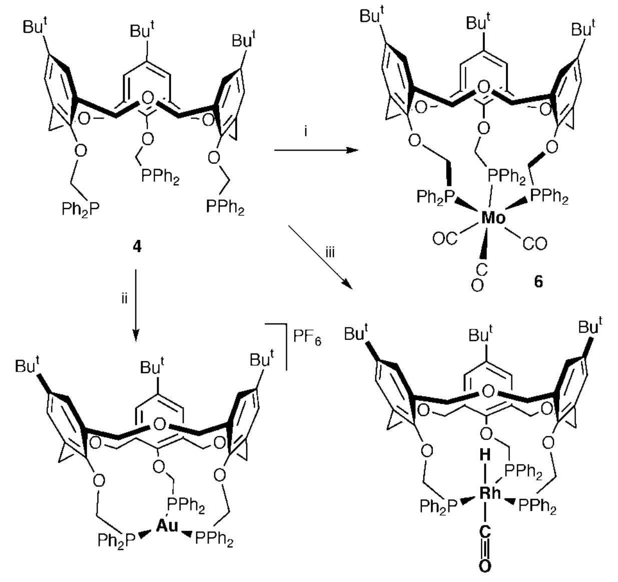


Fig. 1 PLUTON view of triphosphine **5**. For clarity, only the *ipso* carbon atoms of the PPh groups are shown.



Scheme 1 *Reagents and conditions*: i, [Mo(CO)$_3$(cycloheptatriene)], THF, reflux; ii, [Au(THT)(THF)]PF$_6$, CH$_2$Cl$_2$; iii, [Rh(acac)(CO)$_2$], 20 bar H$_2$/CO, toluene, 70 °C.

positions a metal centre across one entrance of the cone. In this case, the trigonal AuP$_3$ fragment strapped across the lower rim exaggerates the conical nature of the calix[3] unit. A similar funnel-shaped silver complex **8**† (not drawn) was also obtained quantitatively from reaction with AgBF$_4$. The room temperature NMR data of both these cationic complexes are in full accord with a C_{3v} symmetrical structure. As deduced from a variable temperature NMR study made with **8,** the threefold symmetry of this complex is only virtual and corresponds in fact to an averaged structure. Indeed, the A$_3$X (X = Ag) pattern observed at 25 °C in the ^{31}P NMR (202.45 MHz) spectrum broadens on decreasing the temperature and eventually changes to an A$_2$BX system, while maintaining finite AgP coupling constants. The C_s symmetry observed at low temperature probably minimizes the strain within two of the three metallomacrocycles formed by complexation, but the exact structure of the complex is not known. Loss of C_3 symmetry at low temperature has previously been observed in a titanium-capped cone homooxacalix[3]arene, but in this case the structural modification appears to be controlled by a stereodynamic process occurring at the metal centre.[13]

A remarkable feature of triphosphine **4** concerns its ability to trap and orientate a linear H–Rh–CO fragment. Thus, treatment of a toluene solution of **4** and [Rh(acac)(CO)$_2$] with 20 bar of H$_2$/CO at 70 °C afforded complex **9**† in *quantitative* yield (Scheme 1). The latter species is characterized by a strong carbonyl absorption band at 1977 cm^{-1} while all NMR data are consistent with a threefold symmetry axis. The ^{31}P NMR spectrum, for example, shows a doublet at δ_P 36.4 (J_{RhP} = 153 Hz) due to the phosphorus atoms with the ^{1}H NMR spectrum displaying a quartet at δ_H −9.70 for the hydrido ligand. The small J_{PH} value (14 Hz) is in full agreement with a trigonal bipyramidal geometry. Two-dimensional ROESY (500 MHz) experiments unambiguously revealed that the hydride lies close to the methylenic Ar*CH*$_2$O groups¶ and to the PCH$_2$ protons. This is a clear indication that the Rh–H bond is directed inside the funnel. This particular orientation of the organometallic fragment is presumably stabilised by weak interactions between the hydride group and the phenolic oxygen atoms that also serve to enlarge the open mouth of the cavity.

As exemplified by complexes **7**–**9**, the tridentate homooxacalix[3]arene **4** facilitates formation of chelate complexes where the phosphine ligands occupy three equatorial sites. This strategy positions a transition metal centre at the bottom of a cone-shaped molecule and, in the case of Rh, leaves an axial coordination site trapped inside the cavity. It is anticipated that the preferential entrapment of Rh–H *vs.* Rh–CO will promote selective insertion reactions with appropriately sized substrates that enter the cavity.

Notes and references

† Satisfactory elemental analyses were obtained for all new compounds. *Selected data* for **2**: δ_H(CDCl$_3$) 6.74 (s, 6H, *m*-ArH), 4.61 (d, $^2J_{PH}$ 3, 3H each, PCH$_2$O), 4.61 and 4.31 (AB q, ^2J 13, 6H each, ArCH$_2$), 1.42 (s, 27H, Bu^t); δ_P(CD$_2$Cl$_2$) 24.9. For **3**: δ_H(CDCl$_3$) 4.75 and 4.43 (AB q, ^2J 10, 2H each, PCH$_2$O), 4.56 (s, 2H, PCH$_2$O), 4.66 and 4.13 (AB q, ^2J 13, 2H each, ArCH$_2$), 4.53 and 4.06 (AB q, ^2J 13, 2H each, ArCH$_2$), 3.95 and 3.79 (AB q, ^2J 13, 2H each, ArCH$_2$), 0.94 and 0.84 (2s, 18H + 9H, Bu^t); δ_P(CDCl$_3$) 26.3 and 25.7. For **4**: δ_H(CDCl$_3$): 6.89 (s, 6H, *m*-ArH), 4.51 (s, 6H, PCH$_2$O), 4.51 and 4.47 (AB q, ^2J 4, 6H each, ArCH$_2$), 1.06 (s, 27H, Bu^t); δ_P(CDCl$_3$) −20.0. For **5**: δ_H(CDCl$_3$) 4.67 and 4.53 (AB q, ^2J 10, 2H each, PCH$_2$O), 4.62 (s, 2H, PCH$_2$O), 4.61 and 4.01 (AB q, ^2J 13, 2H each, ArCH$_2$), 4.42 and 4.12 (AB q, ^2J 13, 2H each, ArCH$_2$), 3.85 and 3.74 (AB q, ^2J 13, 2H each, ArCH$_2$), 1.02 and 0.91 (2s, 18H + 9H, Bu^t); δ_P(CDCl$_3$) −17.4 and −19.9. For **6**: ν_{max} (KBr)/cm^{-1} 1946s, 1854s (C=O); δ_H(CD$_2$Cl$_2$) 6.82 (s, 6H, *m*-ArH), 5.17 (s, 6H, PCH$_2$O), 4.10 and 3.84 (AB q, ^2J 4, 6H each, ArCH$_2$), 1.08 (s, 27H, Bu^t); δ_P(CDCl$_3$) 25.7. For **7**: δ_H(CDCl$_3$) 6.75 (s, 6H, *m*-ArH), 5.05 (s, 6H, PCH$_2$O), 4.47 and 4.25 (AB q, ^2J 4, 6H each, ArCH$_2$), 1.03 (s, 27H, Bu^t); δ_P(CDCl$_3$) 29.7. For **8**: δ_H(CD$_2$Cl$_2$) 6.95 (s, 6H, *m*-ArH), 5.22 (s, 6H, PCH$_2$O), 4.50 and 4.02 (AB q, ^2J 4, 6H each, ArCH$_2$), 1.13 (s, 27H, Bu^t); δ_P(CDCl$_3$) 6.1 (2d, J_{107AgP} 312, J_{109AgP} 360). For **9**: ν_{max}(KBr)/cm^{-1} 1977s (C=O); δ_H(C$_6$D$_6$) 5.15 (s, 6H, PCH$_2$O), 4.70 (H$_A$) and 4.12 (H$_B$) (AB q, ^2J 4, 6H each, ArCH$_2$), 1.13 (s, 27H, Bu^t), −9.70 (q, $^2J_{PH}$ 14, 1H, Rh-H); δ_P(C$_6$D$_6$) 33.4 (d, J_{PRh} 153).

‡ *Crystal data* for **5** C$_{154}$H$_{180}$O$_{17}$P$_6$•3CH$_3$OH•H$_2$O, *M* 2488.98, triclinic, space group $P\bar{1}$, colourless prisms, *a* 13.0120(7), *b* 13.3008(4), *c* 21.468(1) Å, *V* 3687.2(5) Å^3, *Z* 1, D_c 1.12 g cm^{-3}, μ 0.133 mm^{-1}, *F*(000) 1330. Data were collected on a Nonius KappaCCD diffractometer (graphite Mo-Kα radiation, λ = 0.71073 Å) at −100 °C. 27813 reflections collected (2.5 ⩽ θ ⩽ 30.5°), 7778 data with $I > 3\sigma(I)$. The structure was solved using the Nonius (ref. 14) package and refined by full-matrix least-squares with anisotropic thermal parameters for all non-hydrogen atoms except for the phenyl rings attached to P(3), H$_2$O and two MeOH molecules which were refined isotropically. Some disorder was found for the P(3)Ph$_2$ group adopting two possible orientations with equal occupancy. In Fig. 1 one of the two possible orientations is shown. Final results: *R*(*F*) 0.091, *wR*(*F*) 0.122, GOF 1.065, 791 parameters, largest difference peak 1.339 e Å^{-3}. CCDC 182/1368. See http://www.rsc.org/suppdata/cc/1999/1911/ for crystallographic data in .cif format.

§ Extraction percentage of rare-earth picrates by **2** (the rare-earths are ranged according to increasing atomic number) : Y, 4.0; La, 42.0; Pr, 43.0; Nd, 42.5; Sm, 38.5; Eu, 33.5; Gd, 31.5. Conditions: [M(Pic)$_3$]$_{initial}$ = [Ligand]$_{initial}$ 2.5 × 10^{-4} M, *T* 293 K, solvent: CH$_2$Cl$_2$. A separate experiment was performed for each metal.

¶ The Ar*CH*$_2$ protons appear as an AB system, with δ_A 4.70 and δ_B 4.12. Only the signal at δ 4.70 correlates with the hydride.

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